

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 August 2003 (14.08.2003)

PCT

(10) International Publication Number
WO 03/067683 A2

- (51) International Patent Classification⁷: **H01M**
- (21) International Application Number: PCT/US03/03642
- (22) International Filing Date: 6 February 2003 (06.02.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/354,715 6 February 2002 (06.02.2002) US
60/391,626 26 June 2002 (26.06.2002) US
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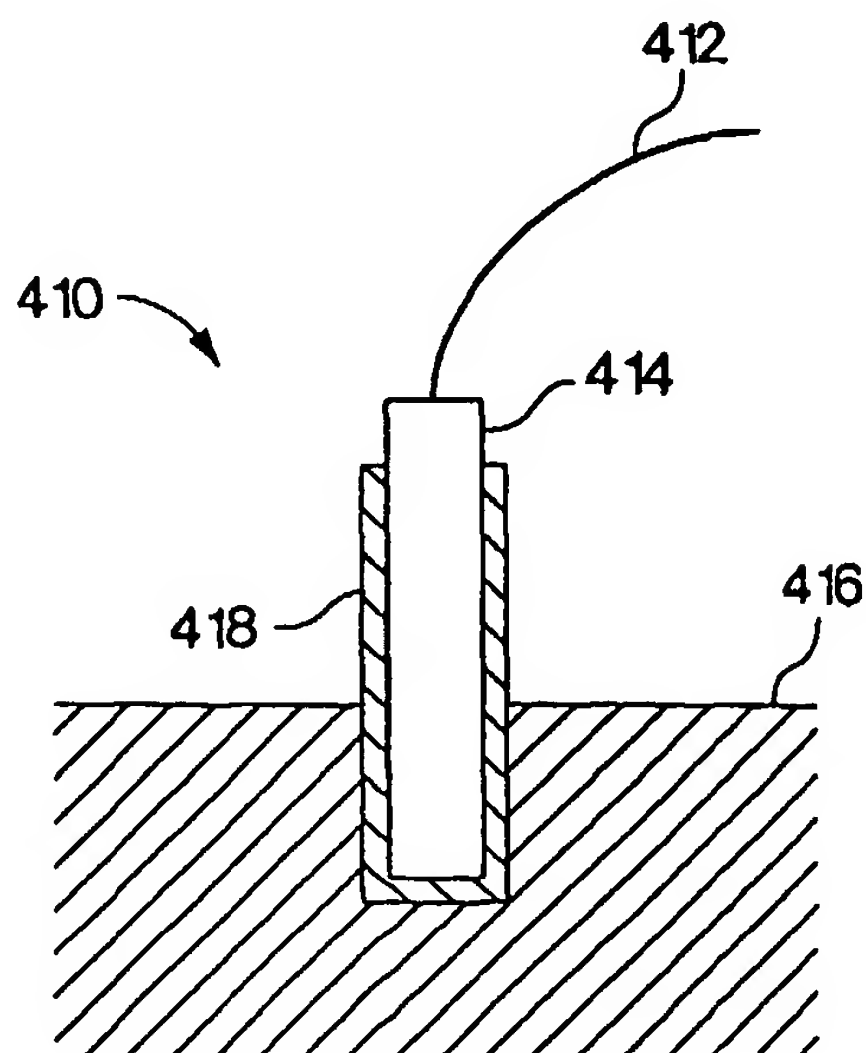
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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: CURRENT COLLECTORS



(57) Abstract: Various aspects of the present invention relate to current collector arrangements and compositions in an electrochemical device. In an electrochemical device used to convert chemical energy via an electrochemical reaction into electrical energy, the electrical energy may be collected via a current collector of the present invention. The electrochemical device may be used anywhere that electrical energy is needed. Examples of electrochemical devices include a fuel cell and a battery; other examples include an oxygen purifier and an oxygen sensor. The current collector may include an electrically conducting core and an electrical connector. In certain embodiments, the electrically conducting core may be made out of a material able to withstand the operating conditions of the electrochemical apparatus, which may include, for example, a liquid anode or cathode, or a reducing or oxidizing environment; in other embodiments, the electrically conducting core may be surrounded and protected from the operating conditions by one or more materials. In some embodiments, additional materials may be used to facilitate electrical communication within the device. For example, an interconnect able to withstand the operating conditions may be used to connect two or more cells within the device.



WO 03/067683 A2

**Published:**

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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CURRENT COLLECTORS

Field of Invention

This invention relates to current collector systems and, more particularly, to
5 current collector systems able to withstand liquid metal environments, environments at
elevated temperatures, or oxidizing or reducing environments.

Background of the Invention

In a fuel cell comprising a solid oxide electrolyte, a cathode reduces oxygen to
10 oxygen ions and an anode oxidizes a fuel accompanied by a release of electrons. The
oxidized fuel combines with the oxygen ions to counteract a resulting flow of released
electrons through an external circuit. The anode is typically not consumed during
operation of the fuel cell. Theoretically, the fuel cell can operate as long as fuel is
supplied to the anode.

15 Electrical output depends on several factors, including the type of fuel used, the
operational temperature, and the electrode and the electrolyte components. To provide a
high electrical output, new materials have been devised that can withstand high
operational temperatures. Such high temperatures may not be practical for many
applications, however. In addition, a combination of currently known materials results in
20 a heavy device, which is not practical for some applications. Attempts to improve the
performance of fuel cells include the discovery of new materials for anode, electrolyte
and cathode components. Each device, however, is generally specific for a certain type
of fuel.

In a metal/air battery, a cathode reduces oxygen to oxygen ions in a similar
25 manner to a fuel cell, but the anode itself oxidizes, the process of which provides
electrons that are released to an external circuit. Thus, the anode is consumed. For
charge balance, the oxidized anode reacts with oxygen ions produced by the cathode.
The battery does not require fuel in order to generate electricity. The battery, however,
has only a defined lifetime as determined by the lifetime of the anode.

30 Attempts have been made by others to combine the attributes of a fuel cell and a
battery. For example, a device may comprise separate battery and fuel cell components,
thus combining the storage capacity of a battery with the longevity of fuel cells. This
arrangement, however, only adds to the weight of the device.

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Summary of the Invention

The present invention relates to current collector systems able to withstand liquid metal environments or environments at elevated temperatures, or oxidizing or reducing environments. The subject matter of this application involves, in some cases, interrelated products, alternative solutions to a particular problem, and/or a plurality of different uses of a single system or article.

In one aspect, the invention comprises an apparatus. In one set of embodiments, the apparatus includes an electrochemical device having a current collector, and an electrical connector in electronic communication with the current collector. In one embodiment, the current collector is defined at least in part by an electrically conducting material having a specific power loss of less than about 100 W/cm^2 .

In another aspect, the invention comprises an electrical device. In one set of embodiments, the electrical device includes a current collector, and an electrical connector in electronic communication with the current collector. In one embodiment, the current collector has at least one portion that is a liquid at temperatures at which the device is designed to operate comprising a metal selected from the group consisting of copper, molybdenum, iridium, palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, chromium, nickel, iron, tungsten, cobalt, zinc, vanadium, gallium, aluminum, and alloys thereof. In yet another embodiment, the current collector is defined at least in part by a material constructed and arranged to conduct electricity when exposed to a reducing environment comprising a liquid metal.

In another set of embodiments, the electrical device includes a current collector defined at least in part by an electrical conductor, and a sheathing material surrounding at least a portion of the electrical conductor. In one embodiment, the sheathing material includes an element selected from the group consisting of scandium, indium, a lanthanide and mixtures thereof. In another embodiment, the sheathing material includes an element selected from the group consisting of scandium, yttrium, titanium, tin, indium, aluminum, zirconium, iron, cobalt, manganese, strontium, calcium, magnesium, barium, beryllium, a lanthanide, chromium, and mixtures thereof.

In yet another set of embodiments, the electrical device includes a current collector having a first liquid metal, a second metal in electrical communication with at

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least a portion of the current collector, and an electrical connector in electronic communication with the current collector.

In another aspect, the invention comprises a method of making any of the embodiments described herein. In yet another aspect, the invention comprises a method
5 of using any of the embodiments described herein.

In another aspect, the invention comprises a method of making a current collector. The method includes the steps of providing a sheathing material having an interior space, positioning an electrically conducting material within the interior space, and positioning a liquid metal within the interior space, wherein the liquid metal is
10 selected from the group consisting of copper, molybdenum, iridium, palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, chromium, nickel, iron, tungsten, cobalt, zinc, vanadium, gallium, aluminum, and alloys thereof.

In yet another aspect, the invention comprises a method of using a current
15 collector. In one set of embodiments, the method includes the step of collecting an electrical current from an electrochemical device having a current collector.

In another set of embodiments, the method includes the step of collecting an electrical current from a current collector having an internal liquid metal selected from the group consisting of copper, molybdenum, iridium, palladium, antimony, rhenium,
20 bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, chromium, nickel, iron, tungsten, cobalt, zinc, vanadium, gallium, aluminum and alloys thereof, where the current collector is constructed and arranged to be positioned as a component of an electrode. In another set of embodiments, the method comprises the steps of allowing at least a portion of a metal
25 that comprises at least a portion of a current collector to melt, and collecting an electrical current from the current collector. In yet another set of embodiments, the method includes the step of collecting an electrical current from a current collector able to remain substantially solid when exposed to a liquid metal at a temperature of greater than about 200 °C or 300 °C. In another set of embodiments, the method comprises the step of
30 collecting an electrical current from a current collector comprising a metal and a sheathing material. In one embodiment, the sheathing material includes an element selected from the group consisting of scandium, indium, a lanthanide and alloys thereof. In another embodiment, the sheathing material includes an element selected from the

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group consisting of scandium, yttrium, titanium, tin, indium, aluminum, zirconium, iron, cobalt, manganese, strontium, calcium, magnesium, barium, beryllium, a lanthanide, chromium, and mixtures thereof. In another set of embodiments, the method comprises the steps of exposing a current collector to a liquid metal having temperature greater than
5 about 200 °C or 300 °C, and eroding the current collector at a rate of less than about 1.8 cm per year. In yet another set of embodiments, the method includes the step of collecting an electrical current from a current collector that is substantially solid while the current collector is exposed to a liquid metal having a temperature of greater than about 200 °C or 300 °C.

10 In another aspect, the invention provides a method including the steps of exposing a cathode current collector to an oxidizing environment, and flowing an agent across a cathode current collector that inhibits oxidation of the cathode current collector.

The invention includes an electrical device in another aspect. The electrical device includes a cathode current collector having an electrical conductor and a
15 sheathing material surrounding at least a portion of the electrical conductor, and a source of a non-oxidizing agent in fluid communication with the cathode current collector. In yet another aspect, the invention provides an apparatus comprising an electrochemical device having a cathode, and a cathode current collector in deformable contact with the cathode. In one embodiment, the current collector has a wire-form shape.

20 In another aspect, the invention includes an electrical stack. The electrical stack includes a first electrochemical device comprising a cathode, a second electrochemical device comprising an anode, and an interconnect in electronic communication with the anode and the cathode. The interconnect also includes a metal that is a liquid at temperatures at which the electrical stack is designed to operate.

25 Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of non-limiting embodiments of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, each identical or nearly identical component that is illustrated in various figures typically is represented
30 by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the

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invention. In cases where the present specification and a document incorporated by reference include conflicting disclosure, the present specification shall control.

Brief Description of the Drawings

5 Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying drawings in which:

Fig. 1 shows a cross-sectional schematic diagram of a device of the present invention, highlighting the electrode and electrolyte components;

10 Fig. 2 shows a cross-sectional schematic diagram of a tubular device of the present invention, highlighting the electrode and electrolyte components;

Fig. 3 shows a cross-sectional schematic diagram of a tubular device of the present invention, highlighting the positioning of solid fuel positioned on the anode;

15 Fig. 4 shows a cross-sectional schematic diagram of a tubular device of the present invention, highlighting the positioning of an inlet positioned on one end of the anode, allowing exhaust to exit the other end of the anode;

Fig. 5 shows a cross-sectional schematic diagram of a planar stack of the present invention which utilizes liquid or gaseous fuels;

Fig. 6 shows a cross-sectional schematic diagram of a planar stack of the present invention which utilizes solid fuels;

20 Fig. 7 shows a three-dimensional schematic representation of the planar stack of Fig. 5;

Fig. 8 shows an interconnect positioned between two tubular devices of the present invention;

25 Fig. 9 shows a scheme of the various electrochemical processes that can be carried out by the anode of the present invention within a single device;

Fig. 10 is a schematic diagram of another embodiment of the present invention;

Fig. 11 is a schematic diagram of another embodiment of the present invention;

Fig. 12 is a cross-sectional view of one embodiment of the invention;

Fig. 13 is a cross-sectional view of another embodiment of the invention;

30 Fig. 14 is a cross-sectional view of another embodiment of the invention;

Fig. 15 is a cross-sectional view of another embodiment of the invention;

Fig. 16 is a cross-sectional view of another embodiment of the invention;

Fig. 17 is a cross-sectional view of another embodiment of the invention;

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Fig. 18 is a cross-sectional view of another embodiment of the invention;
Fig. 19 is a cross-sectional view of another embodiment of the invention;
Fig. 20 is a cross-sectional view of another embodiment of the invention;
Fig. 21 is a cross-sectional view of another embodiment of the invention;
5 Fig. 22 is a cross-sectional view of another embodiment of the invention;
Fig. 23 is a cross-sectional view of another embodiment of the invention;
Fig. 24 is a cross-sectional view of another embodiment of the invention;
Fig. 25 is a cross-sectional view of another embodiment of the invention;
Fig. 26 is a cross-sectional view of another embodiment of the invention;
10 Fig. 27 is a cross-sectional view of another embodiment of the invention; and
Fig. 28 is a cross-sectional view of another embodiment of the invention.

Detailed Description

Various aspects of the present invention relate to current collector arrangements
15 and compositions in an electrochemical device. In an electrochemical device used to
convert chemical energy via an electrochemical reaction into electrical energy, the
electrical energy may be collected via a current collector of the present invention. The
electrochemical device may be used anywhere electrical energy is needed. Examples of
electrochemical devices include a fuel cell and a battery; other examples include an
20 oxygen purifier and an oxygen sensor. The current collector may include an electrically
conducting core and an electrical connector. In certain embodiments, the electrically
conducting core may be made out of a material able to withstand the operating
conditions of the electrochemical apparatus, which may include, for example, a liquid
anode or cathode, or a reducing or oxidizing environment; in other embodiments, the
25 electrically conducting core may be surrounded and protected from the operating
conditions by one or more materials. In some embodiments, additional materials may be
used to facilitate electrical communication within the device. For example, an
interconnect able to withstand the operating conditions may be used to connect two or
more cells within the device.

30

Background on Chemically Rechargeable Anode Electrochemical Devices

The present invention provides new electrochemical devices that display at least
one or any combination of the following advantageous features: (1) a capability for

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chemical recharging; (2) simplified construction; (3) increased electrical output; and (4) a capability for providing a stack of electrochemical devices that afford low mechanical and thermal stresses. Certain aspects of the invention exploit the construction of an anodic material in conjunction with the use of different fuel types. The various
5 embodiments of the present invention also provide novel methods for the generation of electricity.

One aspect of the present invention provides an electrochemical device. In one embodiment, electrochemical devices of the present invention are capable of converting chemical energy, via an electrochemical reaction, into electrical energy to produce an
10 electrical output. Examples of electrochemical devices include a fuel cell and a battery. Other examples include an oxygen purifier and an oxygen sensor.

In one embodiment, the electrochemical device has a dual-mode capability in that the device may operate both as a fuel cell and as a battery. Thus, not only is the anode capable of oxidizing a fuel source and releasing electrons (e.g., as in a fuel cell), but the
15 anode itself is capable of being oxidized with the release of electrons (e.g., as in a battery). As used herein, "oxidizing" and "reducing" (as well as related words such as "oxidation" and "reduction") are given their ordinary definitions as is understood by those of ordinary skill in the art, referring to changes in the oxidation state of the atom or molecule, or equivalently, changes in the electron number.

20 An advantage of this dual-mode capability may be illustrated by the following scenario. A typical prior art fuel cell can produce power so long as there is a supply of fuel. When the fuel supply is exhausted, the electrical output ceases almost instantaneously. This situation may be disastrous especially when a fuel cell device is being used for variable load applications in which replacement fuel is not immediately
25 available. To circumvent this problem, certain prior art fuel cell devices have been provided with a battery back-up. The addition of a separate battery, however, adds weight and complexity to the fuel cell device, which is undesirable especially for variable load applications.

The use of batteries as a sole source of power also has its disadvantages. In a
30 typical battery, electrical power is generated at the expense of anode consumption, as the anode is consumed to release electrons. This anode consumption causes batteries to have a defined lifetime which is dictated, in large part, by the lifetime of the anode. To circumvent this problem, certain prior art electrically rechargeable batteries have been

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developed in which an input of electrons from an outside source reduces the consumed anode and restores the anode to its initial state. However, an external power source is required for electric recharging.

In contrast, the device of the present invention is capable of switching between
5 “battery mode” and “fuel cell mode.” For example, if the fuel supply is exhausted, the device may continue to generate electricity while operating in battery mode thereby eliminating the need for an external battery back-up. Furthermore, when the fuel supply is replenished the device in battery mode may switch back to fuel cell mode if so desired. These features will be discussed more fully below.

10 Another aspect of the invention provides an electrochemical device which comprises an anode constructed of a material such that the anode is a chemically rechargeable anode. As used herein, the term “construct” and similar terms are given their common definitions, and do not encompass accidental, temporary, incidental, or degenerate structures, i.e., structures that do not perform their intended function.

15 A “chemically rechargeable anode” refers to an anode capable of being recharged by the addition of a chemical reductant, as opposed to conventional electrically rechargeable devices. A “chemically rechargeable device” as used herein refers to a device comprising a chemically rechargeable anode. Prior to operation, the device of this aspect of the invention provides an anode having an initial oxidation state. When the
20 device is operated in battery mode, at least a portion of the anode is consumed and electrons are released. A “consumed” anode or portion of the anode refers to an anode having a higher oxidation state than the initial oxidation state i.e., the anode is oxidized. Chemical recharging may be initiated by exposing the portion of the consumed anode to a chemical reductant resulting in that portion being reduced to a more reduced state, such
25 as the initial oxidation state. Thus, it is the chemical reductant, not electricity (as in prior art devices), that, at least in part, recharges the anode. In one embodiment, the chemical reductant alone causes recharging of the anode. In another embodiment, a combination of chemical and electrical recharging results in restoration of the anode. An advantage of chemical recharging is the provision of the recharging species, (i.e., the chemical)
30 located within the device itself. Thus no external recharging species is needed. This feature is particularly desired for use in areas where electrical power sources for electrical recharging may not be readily available.

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Certain metal anodes are capable of existing in more than two oxidation states or in non-integral oxidation states. A metal or alloy comprises metals having a neutral charge. Certain metals can be oxidized to one or more oxidation states, any one of these states being of a sufficient electrochemical potential to oxidize the fuel. Conversely, if that metal is oxidized to its highest oxidation state, it may be reduced to more than one lower oxidation state (at least one having a higher oxidation state than neutral) where the anode is capable of functioning in any of these states. Alternatively, a metal oxide or mixed metal oxide may collectively oxidize fuel where metal ions are reduced by formal non-integer values.

10 In one embodiment, the chemical reductant is the fuel itself. An advantage of this embodiment can be illustrated with the previous scenario, in which the device is operating in battery mode. Upon depletion of the anode, the device may convert back to fuel cell mode where the fuel is consumed to produce electricity. In addition, the fuel may chemically recharge the oxidized anode to its initial state via a chemical reaction. A
15 portion of the fuel reduces the anode and another portion of the fuel is oxidized to generate electricity. When the anode is restored (or a portion restored) to a reduced state, such as its initial state, the device regains its internal "battery back-up" for future emergency situations. The use of the fuel itself as a recharging source provides another advantage in that the device automatically contains the recharging source, thus
20 eliminating the need to store additional chemicals into the device. In other embodiment, however, it may be desired to incorporate another chemical reductant specifically for recharging the anode and having sufficient electrochemical activity to carry out this function.

In one embodiment, the chemically rechargeable device may be configured to
25 allow recharging with electricity in addition to the chemical recharging capability. For certain anode materials and certain fuel types, it may be more feasible to recharge electrically if such an electrical power supply is readily available. For mobile applications, it is preferred that the anode is chemically rechargeable as well for the reasons described previously, e.g. eliminate need to carry a separate battery back-up for a
30 lighter device.

In one embodiment, the anode comprises a liquid, preferably at temperatures for which the device is operable. A liquid is a material which exhibits flow properties. In one embodiment, a liquid is a material which exhibits a tendency to flow in response to

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an applied force under given operating conditions of temperature and pressure. Liquids generally have little or no tendency to spontaneously disperse. Preferably, materials which flow within a time scale that is not visually perceptible by the human eye are generally excluded from this definition.

5 One advantageous feature of a liquid anode is that fuel may be dispersed throughout the anode regardless of the physical state of the fuel, i.e., a gaseous, liquid or solid fuel may be dispersed throughout the anode. It is known that electrical output may be increased by increasing the surface area of an anode. Dispersing fuel throughout the anode allows maximization of the surface area exposed to the fuel. In addition, the
10 liquid may be agitated by stirring or bubbling (or any other agitation methods) to help disperse the fuel throughout the liquid. In one embodiment, agitating the anode has further advantages where the anode undergoes oxide formation when consumed. The oxidized portion of the anode may be displaced with agitation to expose the unoxidized anode portions to the fuel. In contrast, a solid anode would form an oxidized portion at
15 the anode/fuel interface, and the oxidized portion may block the fuel from accessing the anode. Additionally, a liquid anode reduces a need to machine the anode, as the anode may conform to any shape of casing used to house the device components. Where the electrolyte is a solid state electrolyte, the anode may conform to the shape of the electrolyte or at least a portion thereof, maximizing the surface area of contact between
20 the anode and the electrolyte.

 In one embodiment, the device is operable, with the anode in a liquid state, at a temperature of less than about 1500 °C, preferably at a temperature of less than about 1300 °C, more preferably less than about 1200 °C, even more preferably less than about 1000 °C, and even more preferably less than about 800 °C. By "operable", it is meant
25 that the device is able to generate electricity, either as a fuel cell or as a battery with the anode in a liquid state, and the anode may not necessarily be a liquid at room temperature. It is understood by those of ordinary skill in the art that anodic temperature can be controlled by selection of anode materials or in the case of an alloy, composition and percentages of the respective metal components, i.e., composition can affect a
30 melting point of the anode. Other example operating temperature ranges include a temperature between about 200 °C to about 1500 °C, about 300 °C to about 1500 °C, between about 500 °C to about 1300 °C, between about 500 °C to about 1200 °C, between about 500 °C to about 1000 °C, between about 600 °C to about 1000 °C,

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between about 700 °C to about 1000 °C, between about 800 °C to about 1000 °C, between about 500 °C to about 900 °C, between about 500 °C to about 800 °C, and between about 600 °C to about 800 °C.

In one embodiment, the device is operable at a temperature at which any of the solid state components (e.g. a cathode or electrolyte) are not easily susceptible to cracking, i.e., the solid state components should maintain their structural integrity at the operating temperature of the device. In another embodiment, the device is operable at a temperature at which the cathode does not react with the electrolyte. In another embodiment, the device is operable at a temperature at which the anode comprises a liquid. One or any combination of these factors may be practiced independently or in combination, and those of ordinary skill in the art can balance these factors with the knowledge that increasing operational temperatures generally result in an increase in electrical output.

In one embodiment, the anode may be a pure liquid or may have solid and liquid components, so long as the anode as a whole exhibits liquid-like properties.

In one embodiment, the anode comprises a metal. The metal may be a pure metal or may comprise an alloy comprising two or more metals. Upon consumption of a portion of the anode, the portion of the anode is oxidized to form a metal oxide. A mixed metal oxide may be formed in the case where the anode is an alloy. In one embodiment, the metal has a standard reduction potential greater than -0.70 V versus the Standard Hydrogen Electrode (determined at room temperature). These values can be obtained from standard reference materials or measured by using methods known to those of ordinary skill in the art. In another embodiment, where the anode comprises more than one metal, all metals preferably have a standard reduction potential greater than -0.70V versus the Standard Hydrogen Electrode. Balancing the various electrochemical potential requirements can be determined by those of ordinary skill in the art. In certain embodiments, an alloy may be used where at least one of the metals does not have a standard reduction potential greater than -0.70V, but is included in the alloy to enhance flow properties, consistency, or other properties not related to electrochemical potential. In other embodiments, the anode may comprise a mixture of a metal and non-metals to enhance flow properties, consistency, or other properties not related to electrochemical potential.

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In one embodiment, the anode comprises a conducting compound, preferably one that is molten at any of the operating temperatures disclosed herein.

In one embodiment, where the fuel is used to chemically recharge the anode, the oxidation potential of the fuel may dictate the anode composition, i.e., the oxidized state of the anode is of a sufficient electrochemical potential to oxidize the fuel.

In one embodiment, the anode is chemically rechargeable from the oxidized state. For example, where the oxidized state is a metal oxide or mixed metal oxide, the chemical recharging results in restoration (i.e. reduction) of the anode back to being a metal or metal alloy. In another embodiment, the chemical recharging results in reduction of the anode to an oxidation state capable of oxidizing the fuel.

In one embodiment, the anode comprises a metal or alloy comprising at least one of a transition metal, a main group metal, an alkaline metal, an alkaline earth metal, a lanthanide, an actinide and combinations thereof. In another embodiment, the anode comprises material such as copper, molybdenum, mercury, iridium, palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, gadolinium, chromium nickel, iron, tungsten, cobalt, zinc, vanadium, gallium, aluminum, or combinations thereof. For example, the anode may comprise a pure metal such as antimony, indium, tin, bismuth, mercury and lead. In another embodiment, the anode comprises an alloy of at least one element such as copper, molybdenum, mercury, iridium, palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, gadolinium, chromium, nickel, iron, tungsten, vanadium, manganese, cobalt, zinc and combinations thereof. Examples of alloys include 5% lead with remainder antimony, 5% platinum with remainder antimony, 5% copper with remainder indium, 20% lead, 10% silver, 40% indium, 5% copper.

In one aspect of the invention, the anode comprises a material that is different from the fuel composition, thus distinguishing the devices of the present invention from metal/air batteries. Metal/air batteries are sometimes referred to as "fuel cells" because the lifetime of metal/air batteries may be increased by adding more anodic material. These batteries, however, do not provide the benefits of the devices of the present invention, as described herein. In one embodiment, the invention provides a method for energy conversion comprising the step of providing a battery and supplying a fuel to an anode in the battery. The fuel is of a different material than the anode material. This

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embodiment allows the device to operate as a fuel cell and a battery. With other batteries, supplying a fuel that is of a different material than the anode material is an irrelevant step and serves no function.

In one aspect of the invention, the device comprises a source of fuel exposable to the anode. "Exposable to the anode" refers to a capability for delivering fuel to the anode. For example, the fuel may be added directly to the anode. Alternatively, the fuel may be contained in a reservoir and may be deliverable to the anode, when needed, via a conduit leading from the reservoir to the anode. When the device is operating in battery mode, the fuel source may be shut off but remains exposable or capable of being exposed to the anode at a later time when fuel cell mode is desired. Alternatively, the fuel may be in contact with the anode, i.e. dispersed throughout the anode, positioned on a surface of the anode or otherwise contacted with the anode during operation and/or storage. In other embodiments, where the anode is a metal, the fuel may be in contact with metal oxide formed from the anode. The anode may be supplied with a new charge of fuel either continuously or periodically. This may be one viable arrangement for solid fuels. Depending on the physical state of the fuel (i.e., solid, liquid or gas), and other physical properties (powder, viscous liquid, etc.), those of ordinary skill in the art can readily construct a delivery mechanism to expose the fuel to the anode.

Examples of classes of fuels include a carbonaceous material; sulfur; a sulfur-containing organic compound such as thiophene, thiourea and thiophenol; a nitrogen-containing organic compound such as nylon and a protein; ammonia, hydrogen and mixtures thereof. Typically, the fuel selected for the device is mission dependent.

Examples of a fuel comprising a carbonaceous material include conductive carbon, graphite, quasi-graphite, coal, coke, charcoal, fullerene, buckminsterfullerene, carbon black, activated carbon, decolorizing carbon, a hydrocarbon, an oxygen-containing hydrocarbon, carbon monoxide, fats, oils, a wood product, a biomass and combinations thereof. Examples of a hydrocarbon fuel include saturated and unsaturated hydrocarbons, aliphatics, alicyclics, aromatics, and mixtures thereof. Other examples of hydrocarbons include gasoline, diesel, kerosene, methane, propane, butane, natural gas and mixtures thereof. Examples of oxygen-containing hydrocarbon fuels include alcohols which further include C₁-C₂₀ alcohols and combinations thereof. Specific examples include methanol, ethanol, propanol, butanol and mixtures thereof. However, almost all oxygen-containing hydrocarbon fuels capable of being oxidized by the anode

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materials disclosed herein may be used so long as the fuel is not explosive or does not present any danger at operating temperatures.

Gaseous fuels such as hydrogen and SynGas (a mixture of hydrogen and carbon monoxide) may also be used in certain embodiments of the invention.

5 In another aspect of the invention, the electrochemical device is capable of operating with more than one type of fuel. The vast majority of prior art fuel cells are designed to operate with a specific fuel type, usually hydrogen and less often methanol. This aspect of the invention makes it possible to capitalize on the benefits of different fuel types. For example, one type of fuel may provide a higher power output whereas
10 another may provide a lower power output but affords lightweight properties. Enhanced performance may be achieved with one type of fuel, yet another type of fuel recharges the anode more efficiently. Other benefits for using different fuel types may be realized, for example, in situations where the price of one fuel type rises and economics dictate the use of a cheaper fuel. Environmental concerns may also be a deciding factor in changing
15 the fuel type. Short term benefits may be realized, for example, in the situation where the supply of one fuel type is exhausted and only another fuel type is readily available.

In one embodiment, the device comprises a variable source of fuel for at least two different fuels. For example, the source of fuel may comprise at least two different reservoirs for two or more different fuels. Each fuel type may be accessed on demand
20 individually, or in combination. In another embodiment, the source of fuel is capable of being interchanged with a different source of fuel. For example, an electrochemical device running on a gaseous fuel may run with a solid carbonaceous fuel dispersed throughout the anode. Those of ordinary skill in the art can readily devise a device comprising various delivery mechanisms.

25 Examples of electrochemical devices of the invention are illustrated in FIGs. 1 and 2. FIG. 1 shows a cross-sectional schematic diagram of electrochemical device 2 having anode 4 in ionic communication with electrolyte 5. "Ionic communication" refers to a positioning and/or interconnecting of an electrode to an electrolyte to allow ions to migrate between the electrode and electrolyte. When anode 4 is in ionic communication
30 with electrolyte 5, negative ions may migrate from electrolyte 5 to anode 4. An alternative arrangement (not shown here) may be provided where anode 4 is in ionic communication with electrolyte 5 even with an intervening layer of another material disposed between and contacting anode 4 and electrolyte 5. For example, a layer of a

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catalyst may be used as the intervening layer to increase the reaction rate between the oxidized fuel and oxygen anions. Electrolyte 5 is also in ionic communication with cathode 6 to allow negatively charged ions to migrate from cathode 6 to electrolyte 5. In the specific embodiment shown in FIG. 1, the electrodes (anode 4 and cathode 6) and electrolyte 5 are shown as solid-state layers in which electrolyte layer 5 is disposed between and contacting anode layer 4 and cathode layer 6.

Leads (or current collectors) 8a and 8b are in electronic communication with anode 4 and cathode 6 respectively. "Electronic communication" refers to any pathway which provides for the transport of electricity. The electrochemical circuit is completed with external circuit 9 which electrically connect leads 8a and 8b; thus, leads 8a and 8b may be formed from any material able to conduct electricity to and from the device, complete the electrochemical circuit. Circuit 9 is typically a metal wire or any material capable of conducting electricity. In one embodiment, lead 8a may comprise graphite and may serve the double function of collecting current and providing a fuel if at least partially submersed in anode 4.

Inlet 10 is a conduit for introducing fuel to the anode. Inlet 10 may be positioned, at least in part, within anode 4 to disperse fuel throughout the anode efficiently. Alternatively, inlet 10 does not have to contact anode 4 but may be positioned at a minimally close distance to allow all the fuel released through inlet 10 to contact anode 4. Inlet 10 may be further connected to a reservoir (not shown) that comprises a source of fuel with or without the use of a conduit. A variety of reservoirs have been or may be developed for the delivery of solid, gaseous or liquid fuel. For example, the reservoir may comprise a pressurized tank of gaseous or liquid fuel. It is not necessary to provide liquid fuels in pressurized form although pressurization advantageously compacts the fuel volume. Solid fuel may be provided as a powder or other deliverable forms poured, sprayed or otherwise distributed from a reservoir in pure form or as a slurry. Optionally other mechanisms may be attached which forces the fuel from the reservoir through a conduit and through inlet 10.

Not shown in FIG. 1 is a casing for containing and/or protecting device 2. The casing is preferably constructed of a material that may withstand the desired operating temperature. Also not shown in FIG. 1 is a housing to isolate the anode from atmospheric oxygen, and this housing may be the same or different as the casing that contains device 2. In these embodiments, a conduit which penetrates the casing and/or

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housing may be provided for delivering the oxygen-containing flow 7 to cathode 6. The device may further comprise another conduit to release waste products, such as gases or liquids, from the casing and/or housing.

The cathode ionizes oxygen to oxygen ions as represented by the electrochemical half reaction shown in Eq. 1:



This ionization occurs when the device operates in battery or fuel cell mode. The cathode may be exposed to any oxidizing agent, such as air, pure oxygen or any oxygen-containing gas 7, at atmospheric pressures or greater. Alternatively, the device may include an inlet to expose cathode 6 to the oxygen-containing gas 7. Typically, oxygen is reduced at an interface between cathode 6 and the oxygen-containing gas 7. Cathode 6 preferably comprises a material which allows oxygen ions to migrate through cathode 6 and access electrolyte 5.

When the fuel cell operates in battery mode, the anode itself is consumed as represented by the electrochemical half reaction of Eq. 2:

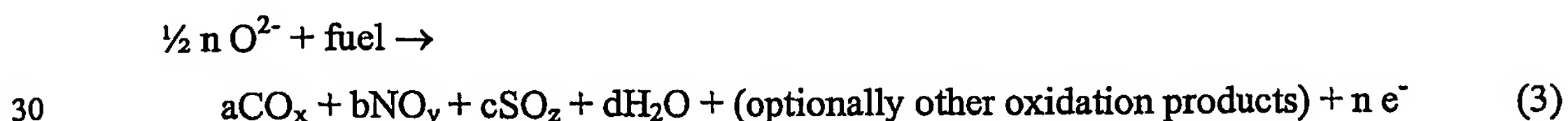


20

where M represents a metal or metal alloy (and accordingly, M^{n+} represents an oxidized metal or alloy), “e⁻” denotes an electron, and n is greater than or equal to 1, depending on the metal or metal alloy. M^{n+} is typically present as a metal oxide (or mixed metal oxide). As described previously, the portion of the anode that is oxidized, as shown in Eq. 2, forms an oxidized portion on or within the anode.

25

When the device is in fuel cell mode, a variety of reactions may occur. The fuel is oxidized at the anode, thereby releasing electrons, as represented in Eq. 3:



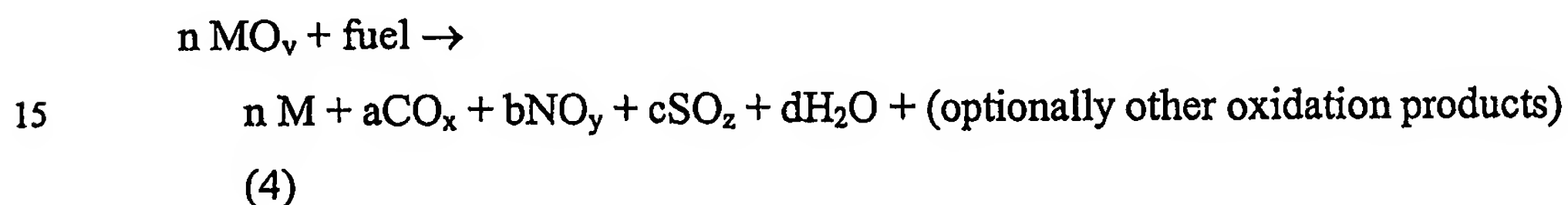
30

The oxygen anions shown in Eq. 3 are, for the most part, supplied by the cathode reaction of Eq. (1). Eq. 3 is intended to represent some of the various possible oxidation

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products. The coefficients a, b, c, d, x, y, and z may be the same or different and each are greater than or equal to zero and their values depend on the type of fuel used, and at least one of a, b, c, d, x, y, and z will be greater than zero. The coefficient "n" is greater than 0. The fuel may comprise a combination of "a" carbon atoms and/or "b" nitrogen atoms and/or "c" sulfur atoms and/or d hydrogen atoms, etc. For example, CO_x may represent CO₂, CO or a mixture thereof. If hydrogen is the fuel, water is the sole oxidation product. Not all possible oxidation products are represented by Eq. 3 and depending on the composition of the fuel, those of ordinary skill in the art can determine the resulting oxidation product. Thus, a net reaction of the anode in fuel cell mode involves oxidation of the fuel with no consumption of the anode.

Without wishing to be bound by any theory, the recharging of the anode by the fuel is represented by Eq. (4).



The reaction of Eq. (4) is similar to that of Eq. (3), except the oxygen anions are provided, at least in part, by the metal or mixed metal oxide, "MO_v" where "v" is greater than 0.

In one embodiment, the device is capable of electrical output of at least about 10 mWatt/cm², preferably at least about 50 mWatt/cm², preferably at least about 100 mWatt/cm², even more preferably at least about 200 mWatt/cm², even more preferably at least about 300 mWatt/cm², and even more preferably at least about 500 mWatt/cm².

In one embodiment, the cathode is a solid state cathode. Examples of solid state cathodes include a metal oxide and a mixed metal oxide. Specific examples include tin-doped In₂O₃, aluminum-doped zinc oxide and zirconium-doped zinc oxide. Another example of a solid state cathode is a perovskite-type oxide having a general structure of ABO₃, where "A" and "B" represent two cation sites in a cubic crystal lattice. A specific example of a perovskite-type oxide has a structure La_xMn_yA₂B_bC_cO_d where A is an alkaline earth metal, B is selected from the group consisting of scandium, yttrium and a lanthanide metal, C is selected from the group consisting of titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, hafnium, aluminum and

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antimony, x is from 0 to about 1.05, y is from 0 to about 1, a is from 0 to about 0.5, b is from 0 to about 0.5, c is from 0 to about 0.5 and d is between about 1 and about 5, and at least one of x, y, a, b and c is greater than zero. More specific examples of perovskite-type oxides include LaMnO_3 , $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$, $\text{La}_{0.84}\text{Ca}_{0.16}\text{MnO}_3$, $\text{La}_{0.84}\text{Ba}_{0.16}\text{MnO}_3$,
 5 $\text{La}_{0.65}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_3$, $\text{La}_{0.79}\text{Sr}_{0.16}\text{Mn}_{0.85}\text{Co}_{0.15}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$,
 $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$,
 $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$, $\text{La}_{0.6}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Al}_{0.2}\text{O}_3$, $\text{La}_{0.84}\text{Sc}_{0.16}\text{MnO}_3$, $\text{La}_{0.84}\text{Y}_{0.16}\text{MnO}_3$,
 $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$, LaCoO_3 , $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$, $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$, or other LSM materials. As used herein, "LSM" refers to any lanthanum-strontium-manganese oxide, such as
 10 $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$. In other embodiments, the ceramic may also include other elements, such as titanium, tin, indium, aluminum, zirconium, iron, cobalt, manganese, strontium, calcium, magnesium, barium, or beryllium.

Other examples of solid state cathodes include LaCoO_3 , LaFeO_3 , LaCrO_3 , and a LaMnO_3 -based perovskite oxide cathode, such as $\text{La}_{0.75}\text{Sr}_{0.25}\text{CrO}_3$, $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.9}\text{CrO}_3$,
 15 $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ or $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, where Ln may be any one of La, Pr, Nd, Sm, or Gd.

Alternatively, the cathode may comprise a metal, for example, the cathode may comprise a noble metal. Example metal cathodes include platinum, palladium, gold, silver, copper, rhodium, rhenium, iridium, osmium, and combinations thereof.

20 The electrolyte allows conduction of ions between the cathode and anode. The electrolyte allows migration of oxygen ions from the cathode to the anode. In one embodiment, the electrolyte is a solid state electrolyte. Example solid state electrolytes include a metal oxide and mixed metal oxides.

An example of a solid state electrolyte is an electrolyte having a formula
 25 $(\text{ZrO}_2)(\text{HfO}_2)_a(\text{TiO}_2)_b(\text{Al}_2\text{O}_3)_c(\text{Y}_2\text{O}_3)_d(\text{M}_x\text{O}_y)_e$ where a is from 0 to about 0.2, b is from 0 to about 0.5 c is from 0 to about 0.5, d is from 0 to about 0.5, x is greater than 0 and less than or equal to 2, y is greater than 0 and less than or equal to 3, e is from 0 to about 0.5, and M is selected from the group consisting of calcium, magnesium, manganese, iron, cobalt, nickel, copper, and zinc. More specifically, examples of solid state electrolytes
 30 include (ZrO_2) , $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}$, $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$, $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.05}$,
 $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}(\text{TiO}_2)_{0.10}$, $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}(\text{Al}_2\text{O}_3)_{0.10}$,
 $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{Fe}_2\text{O}_3)_{0.05}$, $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{CoO})_{0.05}$, $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{ZnO})_{0.05}$,

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$(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{NiO})_{0.05}$, $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{CuO})_{0.05}$, $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{MnO})_{0.05}$ and ZrO_2CaO .

Other examples of solid state electrolytes include a CeO_2 -based perovskite, such as $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ or $\text{Ce}_{1-x}\text{Gd}_x\text{O}_2$ where x is no more than about 0.5; lanthanum-doped ceria, such as $(\text{CeO})_{1-n}(\text{LaO})_n$ where n is from about 0.01 to about 0.2; a LaGaO_3 -based perovskite oxide, such as $\text{La}_{1-x}\text{A}_x\text{Ga}_{1-y}\text{B}_y\text{O}_3$ where A may be Sr or Ca, B may be Mg, Fe, Co and x is from about 0.1 to about 0.5 and y is from about 0.1 to about 0.5 (e.g. $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$); a PrGaO_3 -based perovskite oxide electrolyte, such as $\text{Pr}_{0.93}\text{Sr}_{0.07}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_3$ or $\text{Pr}_{0.93}\text{Ca}_{0.07}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_3$; and a $\text{Ba}_2\text{In}_2\text{O}_5$ -based perovskite oxide electrolyte, such as $\text{Ba}_2(\text{In}_{1-x}\text{Ga}_x)_2\text{O}_5$ or $(\text{Ba}_{1-x}\text{La}_x)\text{In}_2\text{O}_5$, where x is from about 0.2 to about 0.5.

In one embodiment, the electrochemical device is a solid-state device which comprises solid-state cathode and electrolyte components as described previously. Preferably, the anode is a liquid as described previously.

In one embodiment, the device provides an electrolyte having small thicknesses. A small thickness provides at least one of many advantageous features: (1) efficient migration of ions; (2) provision of the oxygen-containing gas at relatively low pressures; and (3) facile design of miniature devices. In one embodiment, the electrolyte has a thickness of less than about 200 μm , and more preferably less than about 100 μm .

FIG. 1 shows a cross-section of a device in which each component may be provided as a flat layer or a shaped layer. For example, FIG. 1 may also represent a cross-section of a shaped device such as a tubular device. By "shaped device" it is meant that the electrode-electrolyte configuration may be provided as any shape besides a flat layer, as known to those of ordinary skill in the art.

FIG. 2 shows a schematic cross-section of one type of shaped layer, i.e. tubular device 12. Device 12 of FIG. 2 has similar components as device 2 of FIG. 1. In FIG. 2, anode 14 is centrally positioned within and enclosed by electrolyte 15. Encircling electrolyte 15 is cathode layer 16. Leads 18a and 18b contact anode 14 and cathode 16 respectively. Inlet 20, for introducing gaseous or liquid fuels if applicable, is shown submersed in the anode but may be positioned anywhere that allows the fuel to be exposable to anode 14. Optionally, cathode layer 16 may be positioned within a casing to protect cathode layer 16 from breakage, as cathode layer 16 is typically provided as a thin layer. The casing may be sufficiently porous to allow oxygen to access cathode

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layer 16. Alternatively, device 12 may further comprise one or more conduits (not shown) to provide an oxygen-containing gas flow 17 to the cathode, or for removing exhaust from the device (e.g., gases, unreacted fuels, reaction products, and the like).

Another aspect of the present invention provides a housing for the anode comprising a solid-state electrolyte material. This feature provides an efficient design for an electrochemical device as the solid-state electrolyte serves two functions: (1) as a medium for the transport of ions to and from the electrodes; and (2) for containing a liquid anode. Design efficiency is advantageous, particularly when stacks of electrochemical devices are employed. In this aspect, a separate housing is eliminating, thus reducing cost of materials and resulting in a more lightweight device. The electrolyte housing may be constructed solely of electrolyte material, or partially of electrolyte material. Ideally, the housing should comprise enough electrolyte material to span a dimension of the anode, such as in FIG. 2 (electrolyte makes up essentially the entire housing) or FIGs. 3 and 4 (electrolyte makes up wall 25 only). Of course, the electrolyte material may be of any dimension, depending on the electrical output and/or economic requirements. Generally, efficient device design results from maximizing the surface area which provides ionic communication between the electrode/electrolyte components.

Alternatively, the housing may comprise a mixture of electrolyte and non-electrolyte materials. Preferred non-electrolyte materials in this mixture have thermal expansion coefficients substantially similar to the electrolyte material. In one embodiment, the thermal expansion coefficients of the electrolyte and non-electrolyte materials differ by less than about 30% at a temperature of less than about 1500°C, preferably less than about 20% and more preferably less than about 10%. Example non-electrolyte materials that may be included in this mixture include α -Al₂O₃. As used herein, the "thermal expansion coefficients" (e.g., linear and volumetric) are given their usual definitions as is understood by those of ordinary skill in the art. The "overall" or "total" thermal expansion coefficient is also given its usual definition understood by those of ordinary skill, i.e., referring to the combined net thermal expansion of a material formed from multiple substances, each of which may have different individual thermal expansion coefficients.

In one embodiment, an electrolyte housing is surrounded and in ionic communication with a cathode material. In this embodiment, the cathode conforms to

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the shape of the electrolyte, or at least to the dimension of the electrolyte which spans a dimension of the anode. FIG. 2 shows cathode 16 in conforming contact with electrolyte 15 which also functions as a housing for the anode. FIG. 3 shows another embodiment, where cathode 26 only surrounds the walls of electrolyte 25, leaving base 29 free of
5 contact with cathode material.

Another advantageous feature of a liquid anode in certain embodiments involves the ability of the anode to act as a sealant precursor to seal a flaw in the device. In this embodiment, the device is "self-repairing," and does not require any active human intervention for the repair. For example, when a solid state electrolyte develops a crack
10 or other flaw, a liquid metal anode may flow to substantially cover and/or substantially fill the crack. Subsequently, the anode may react with oxygen to form a metal oxide (or mixed metal oxide in the case where the anode is an alloy). The resulting oxide formed substantially conforms to the crack due to the flow properties of the initially liquid anode. Even though the present device minimizes thermal and mechanical stresses due
15 to the liquid properties of the anode, the self-repairing capability helps to ensure the integrity of the device, particularly when repair is not feasible, e.g. during operation of the system.

FIGs. 3 and 4 display various methods of exposing an anode to a source of fuel. FIG. 3 shows a cross-sectional schematic diagram of a tubular device 22 having
20 electrolyte 25 in ionic communication with anode 24 and cathode 26. Base 29 may be of the same material as electrolyte 25, or of a different material and the connection between electrolyte 25 and base 29 may be integral or non-integral. Lead 28a (which may comprise a graphite material) is submersed in anode 24 and is electrically connected to lead 28b which is in electronic communication with cathode 26. Fuel 23 is shown
25 positioned on top of anode 24 and may either be consumed in this manner or may be dispersed throughout the anode. This arrangement is useful in the situation where the fuel is not easily transferred from an inlet, such as in the case of certain solid fuels. Optionally, the device may further comprise a mechanism for urging fuel 23 towards the anode as fuel 23 is consumed. An urging mechanism allows maximum contact surface
30 area between fuel 23 and anode 24. Examples of urging mechanisms include various mechanical devices, such as a spring, a clamp, a rod or a diaphragm, or other urging mechanisms known to those of ordinary skill in the art. Mixing or agitation may also accomplish the urging.

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FIG. 4 shows a cross-sectional schematic diagram of tubular device 32, featuring another position of inlet 40 with respect to device 32. Device 32 comprises electrolyte 35 in ionic communication with anode 34 and cathode 36. Base 39 may be of the same or a different material as electrolyte 35 and the connection between electrolyte 35 and base 39 may be integral or non-integral. Lead 38a is partially submersed in anode 34 and does not extend all the way to base 39. Inlet 40 penetrates through base 39 to the extent that a space exists between inlet 40 and lead 38a. Upon release of fuel 41 into anode 34 through inlet 40, the fuel may be readily dispersed throughout a maximum portion of anode 34. Another advantage to this arrangement is that any waste products will naturally travel to an aperture opposite, or at a distance from inlet 40, for example, areas 42 in which anode 34 contacts the atmosphere. Alternatively, the device of the present invention may further comprise an exhaust conduit to remove any waste from the device.

Certain prior art devices require operating temperatures of greater than 1000°C. It is generally desired to lower these operating temperatures to minimize thermal energy provided to the device. Exceedingly high temperatures may also lead to electrolyte or cathode cracking or the formation of other flaws in the device. In addition, rapid start-up heating times provides an advantage in the situation where electrical power is required quickly. The higher the operating temperature, however, the greater the time needed for start-up heating of the device.

Thus, another aspect of the present invention provides an electrochemical device comprising an anode comprising a liquid at a temperature of no more than about 1000°C. The ability to provide a liquid anode at lower operating temperatures, such as a temperature below 1000°C, reduces a temperature range required for start-up heating. In addition to reducing start-up heating times, lower temperatures afford a more hospitable environment for maintaining the integrity of an interface between different components such as the anode/electrolyte or electrolyte/cathode components.

Another aspect of the present invention provides an electrochemical device comprising an anode and an intermittent fuel source deliverable to the anode to produce a continuous electrical output from the device. "Intermittent fuel source" refers to any fuel source arranged to allow cessation between a period of delivery of the fuel to the anode. In one embodiment, the cessation may be periodic or random. Cessation may be a multiple occurrence or a one-time occurrence. It is a feature of this aspect of the invention that even with this cessation of fuel delivery a continuous electrical output is

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produced. In one embodiment, an intermittent fuel source may be used when the device is switched from fuel cell mode to battery mode where fuel is not delivered to the anode. When fuel is supplied to the device, electricity may be generated via fuel cell operation. Ceasing delivery of fuel to the anode causes the device to switch to battery mode for
5 continuous generation of electricity. An electrical device may be manufactured, using the methods and materials described herein, to derive power continuously while experiencing minimal or almost no shut down time as the electrical device switches between fuel cell and battery modes. During intermittent fuel delivery, the fuel source may also be changed or replenished.

10 In one embodiment, switching from fuel cell mode to battery mode and vice versa occurs automatically. For example, the device of the present invention may operate in fuel cell mode until the fuel is exhausted. Automatic switching is demonstrated when the anode begins to oxidize, thereby releasing electrons, i.e., the device automatically operates in battery mode. In one embodiment, the switching may
15 occur by simply shutting off fuel delivery to the anode or turning on the fuel source. Alternatively, a switch may be constructed which stops/starts introduction of fuel to the anode. Other switching mechanisms can be readily envisioned by those of ordinary skill in the art.

In one embodiment, the device may operate simultaneously in fuel cell and
20 battery mode. In this embodiment, fuel consumption and fuel oxidation by the anode occur simultaneously. This may occur when fuel is supplied to the anode at a low flow rate and/or in low amounts. Alternatively, simultaneous fuel cell and battery operation may inherently occur when fuel is supplied to the device. Switching between fuel cell and battery mode may occur, not as a sharp on/off event, but gradually as the amount of
25 fuel supplied to the anode is increased or decreased.

Another aspect of the invention provides an electrochemical device comprising an anode and a source of fuel exposable to the anode. The anode is constructed of a material such that the device is capable of producing electricity by using the anode (the anode is included in a circuit in which the electricity is produced) in both the presence of
30 fuel without anode consumption (or without net anode consumption, i.e., less anode is consumed than regenerated) and in the absence of fuel. In one embodiment, a device “capable of producing electricity involving the anode in the presence of fuel without anode consumption” refers to generation of electricity via fuel cell operation.

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Conversely, the same anode may deliver electrons to the device without exposure to fuel in which the anode is consumed, such as when the device operates in battery mode. In one embodiment, the electrochemical device is a fuel cell/battery hybrid capable of operating in either fuel cell or battery mode, while producing a continuous electrical
5 output.

Another aspect of the present invention provides a stack of electrochemical devices. Electrical output may be multiplied by supplying a number of devices as described above into one system. For variable load applications, it is usually desired that the stack be lightweight and capable of miniaturization. FIG. 5 shows an example of a
10 stack 100 of planar electrochemical devices. Each device in stack 100 comprises an anode 104 in ionic communication with electrolyte 105. Electrolyte 105 in turn is in ionic communication with cathode 106. Stack 100 further includes an inlet 110 for liquid or gaseous fuel to be provided to each device via guide 111. Inlet 112 allows oxygen to be supplied via guide 113 to each cathode 106. Conduit 114 and outlet 115
15 serve to remove any exhaust gases from stack 100. The multi-device system is positioned within casing 102. Stack 100 further includes preheating chamber 116 to heat each device to an operational temperature.

In this aspect, a liquid anode is particularly advantageous due to its moldable properties. The liquid may function as a seal between each device. Moreover, the liquid
20 provides a soft contact between the liquid anode and the adjacent device to reduce mechanical and thermal stresses between the devices.

As used herein, "soft contact," "deformably contact," and similar terms generally refer to contact between two components in which the two components are able to maintain contact regardless of changes in the shape or size of the components, for
25 example, expansion or contraction due to a change in temperature. Thus, the components are able to move, expand, contract, etc. while maintaining contact. Thus, a liquid in contact with a solid surface is an example of two materials in deformable contact. Other examples of soft or deformable contact include gels or other viscoelastic materials or fluids, or solid materials having shapes able to deform or otherwise be
30 altered while maintaining contact with a second component, for example, a brush (where each bristle may have only intermittent contact, but contact as a whole is maintained). Wire or wire-like devices may be particularly useful in some embodiments of the invention to maintain deformable contact between two or more components. As used

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herein, an object having a “wire-form,” for example, may have the form of a single wire, several wires such as in a brush having bristles that maintain deformable contact, one or a bundle of wires such as in a braid or a strand (for example, which may be twisted together). Other examples include a woven pattern of wires such as in a felt, a fabric, a spring, a knot, or the like. The wire-form object may also be entangled with other objects, for example, as in a knot or a loop. The wire-form shape may allow, for example, easier component fabrication or replacement (e.g., only a portion of the wire-form shape may be removed).

FIG. 5 shows each device in the stack arranged and positioned in a repeat array to arrange identical components in the same orientation. This arrangement may relieve stresses on each device, particularly taking advantage of the soft contact provided by the anode. A variety of arrangements of the devices in the stack can be envisioned to maximize the number of devices that receive fuel from guide 111.

In other embodiments, the devices in the stack may be arranged in series, parallel or may comprise a series-parallel configuration.

The stack need not necessarily be arranged in planar configuration and may be arranged in any array, e.g. such as a rectangular or hexagonal array.

Another advantageous feature of the liquid anode is that by positioning a liquid adjacent a solid component, a non-permanent seal is formed. This non-permanent attachment removes a need to add further components to hold each device adjacent to each other such as adhesives or mechanical attachments. In one embodiment, the casing may provide a series of slots. Each device may simply be guided through the slots to provide the stack. In the event of a malfunction of an individual device, the malfunctioning device may be removed and easily replaced with a new device. For other prior art devices, when one individual device malfunctions, either the permanent seal would have to be broken to replace the individual device or the entire stack will need to be repaired. Of course, other embodiments may provide a permanent seal in addition, depending on the application.

FIG. 6 shows an alternative example of a stack utilizing solid fuel. FIG. 6 shows stack 120 having anode 124 positioned adjacent electrolyte 125 which in turn is positioned adjacent cathode 126. Inlet 132 directs oxygen to individual devices via conduit 133. Solid fuel 130 is positioned within anode 124. Solid fuel 130 may also act as a lead to collect electricity from the anode. Each device may be positioned within

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casing 122. Casing 122 may further comprise inlets to provide more solid fuel to the device, or a reservoir for additional solid fuel sources. Each device in stack 120 may be tubular or planar.

In one embodiment, the stack may further comprise an interconnect positioned
5 adjacent the anode of a first device and the cathode of the second device. An interconnect has an air flow pattern to allow oxygen flow in or out of the stack. In addition, an interconnect may convey electrical currents and/or thermal energy away from each device. Preferably, the interconnect has sufficient electrical conductivity and thermal conductivity to achieve this function. To reduce the likelihood of forming cracks in the
10 device, it is preferred that the interconnect and cathode have similar thermal coefficients. In one embodiment, respective thermal expansion coefficients of the cathode and interconnect differ by less than about 30% at a temperature of less than about 1500°C, preferably less than about 20% and more preferably less than about 10%. In one embodiment, the interconnect comprises substantially the same material as the cathode,
15 and thus the respective thermal coefficients would theoretically differ by about 0%.

Referring back to FIGs. 5 and 6, interconnects 107 and 127 are shown as being positioned adjacent cathodes 106 and 126, respectively, and the adjacent anodes. FIG. 7 shows a close-up of a stack of FIG. 5. Stack 100 features interconnect 107 positioned adjacent cathode 106. Interconnect 107 is also positioned adjacent an anode.

20 FIG. 8 shows another example arrangement for connecting two tubular devices of the invention together to form a stack via an interconnect. In FIG. 8, stack 140 comprises individual units each comprising anodes 144a and 144b positioned adjacent and within electrolyte layers 145a and 145b, respectively. Cathodes 146a and 146b are provided as a layer which coats at least a portion of electrolytes 145a and 145b. Fuel
25 sources 150a and 150b may be positioned adjacent anodes 144a and 144b. Where the fuel is a solid fuel, fuel sources 150a and 150b may comprise a solid rod, such as graphite. In addition, the solid rod may also function as a current collector.

Alternatively, for liquid, gaseous or solid powder fuels, fuel sources 150a and 150b may comprise an inlet positioned within or near anodes 144a and 144b to guide and disperse
30 the fuels throughout anodes 144a and 144b. In any situation, a lead would be required to be positioned in anode 144b and lead 154 may be positioned adjacent cathode 146a. Interconnect 152 is positioned adjacent electrolyte layer 145a and cathode layer 146b. To allow interconnect 152 to contact anode 144a, holes may be provided in a portion of

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electrolyte 145a which contacts interconnect 152. Thus, the anode 144a may flow through the holes to eventually contact interconnect 152. FIG. 8 shows tubular arrangements, but those of ordinary skill in the art can readily design an analogous planar device, in light of the description provided herein.

5 As discussed previously, typical fuel cell interconnects include a gas flow pattern. In one embodiment, an interconnect of the present invention is free of a gas flow pattern, particularly when used with a liquid anode. Because fuel and waste are dispersible throughout the anode and may enter or exit each device via the liquid anode, a gas flow pattern is not essential for the interconnect of the present invention. It is understood that
10 other fuel types may still require an interconnect with a gas flow pattern for enhanced device performance.

As discussed previously, the interconnect is positioned adjacent a liquid anode, thus reducing many problems associated with thermal coefficients mismatches that may arise as the device is heated to high temperatures. Accordingly, it has been discovered
15 that such moldability of the liquid anode allows the interconnect to have much thinner dimensions than many prior art interconnects. This allows interconnects to be more lightweight and less expensive and these benefits may be extended to the manufacturer of the device.

Thus, the interconnect of the present invention may provide at least one of the
20 following advantages: (1) a reduction in weight by at least 20%, preferably by at least 30% and more preferably by at least 40% compared to prior art interconnects; (2) elimination of intricate, machined gas flow patterns, which reduces the cost and manufacture time; and (3) rapid and repeated start-up heating of the stack due to the minimal thermal and mechanical stresses resulting from contact with adjacent anode and
25 cathode materials.

FIG. 9 shows a schematic diagram summarizing various electrochemical processes that may be carried out by the anode of the present invention. In FIG. 9, anode 200 is represented as "M" in which anode 200 comprises a metal or metal alloy. Eq. 202 of FIG. 9 schematically represents anode 200 functioning as a battery. In Eq. 202, anode
30 200 combines with "y" moles of O^{2-} produced from a cathode. In battery mode, anode 200 releases electrons resulting in the oxidation of M to form a metal or mixed metal oxide, M_xO_y . Eq. 203 schematically shows the chemical rechargeability of the anode which, in the presence of fuel, is reduced back to metal anode 200. In Eq. 203, it is the

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metal oxide that combines with the fuel to produce fuel oxidation products. " M_xO_y " should be of a sufficient electrochemical potential to be reduced by the fuel. Without wishing to be bound by any theory, the combination of Eqs. 202 and 203 schematically illustrates the process undergone by anode 200 when operating in fuel cell mode, in which there is no net consumption of anode. Thus, FIG. 9 shows the capability of anode 200 to: (1) be oxidized in the absence of a fuel and produce electricity, as shown in Eq. 202; (2) regenerate from a corresponding metal oxide, as shown in Eq. 203; and (3) oxidize fuel with no net consumption of the anode, as represented by Eqs. 202 and 203.

Accordingly, another aspect of the present invention provides a method for energy conversion. The method involves providing an electrochemical device comprising an anode, such as any anode described herein. The method also involves causing electricity to be produced when the anode is exposed to a fuel, such that electricity is produced without anode consumption (i.e. anode acts as a catalyst). In one embodiment, this step is exemplified by Eqs. 202 and 203 of FIG. 9. The method also involves causing electricity to be produced in the device in the absence of fuel provided to the anode. This step is distinguished from other devices which provide a back-up battery source having another anode, in the event the fuel supply is exhausted. The present invention allows the same anode to cause electricity to be produced in the presence of a fuel (i.e., when in fuel cell mode) and to cause electricity to be produced in the absence of the fuel. In one embodiment, this step is exemplified by Eq. 202 of FIG. 9.

In one embodiment, either step of causing electricity to be produced in the presence or absence of a fuel involves providing an electrolyte in ionic communication with the anode and a cathode in ionic communication with the electrolyte. These steps may also involve directing an oxygen-containing gas flow to the cathode. In one embodiment, the causing steps may also include heating the device from a temperature of about 300 °C to about 1500 °C, or within other temperature ranges as described previously. Preferably, the chosen temperature range involves producing the anode in a liquid state.

In the embodiment where electricity is produced in the absence of the fuel, the anode is typically consumed. Thus, in one embodiment, the method further comprises providing fuel to the anode to chemically recharge the anode. In one embodiment, this step is exemplified by Eq. 203 of FIG. 9.

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Another aspect of the present invention provides a method for energy conversion. The method involves providing an anode and delivering a fuel to the anode intermittently while producing a continuous electrical output by using the anode. As described previously, "intermittently" may involve any cessation of fuel delivery to the anode.

5 "Producing a continuous electrical output by using the anode" refers to use of the anode continuously, even though fuel is provided to the anode intermittently.

A device comprising a fuel cell and a separate battery back-up is excluded from this aspect of the invention, because when fuel is supplied, the anode of the fuel cell is used to produce electricity. When fuel delivery ceases in favor of the battery backup, the
10 anode of the battery and not the anode of the fuel cell, is used to produce electricity. Thus, the anode of the fuel cell is not used continuously in the continuous production of electricity.

Another aspect of the present invention provides a method involving providing an anode and causing a portion of the anode to be oxidized such that electricity is produced.
15 In one embodiment, this causing step occurs when the anode is operated as a battery, as exemplified by Eq. 202 of FIG. 9. The "portion of the anode" is described as follows. Initially, the portion of the anode that is immediately adjacent the electrolyte is oxidized, as this portion represents the shortest diffusion pathway by which oxygen ions released by the cathode may access the anode. As device operation continues, this oxidized
20 portion grows from the anode/electrolyte interface toward the bulk of the anode, as the anode continues to be consumed.

At any stage of anode consumption, either initially or when the entire anode has been consumed (i.e. at least a portion of the anode is consumed), the method involves exposing the oxidized portion of the anode to a chemical reductant such that the oxidized
25 portion is reduced. In one embodiment, reducing this oxidized portion regenerates the anode to its initial state. In one embodiment, the anode is a metal which is oxidized to a metal oxide, and exposure of the metal oxide to a chemical reductant results in re-formation of the metal anode or to an oxidation state capable of oxidizing the fuel. In one embodiment, the chemical reductant is a fuel. This is advantageous in that the
30 device does not require any new materials as the fuel available is capable of reducing the oxidized portion of the anode to the initial state of the anode.

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In one embodiment, the reduced portion, which results from reducing the oxidized portion, is capable of functioning as an anode again. "Functioning as an anode" involves either the operation of the anode as a battery or a fuel cell.

Another aspect of the invention provides a method for energy conversion, comprising the step of providing a device comprising a liquid metal anode. A portion of the anode is oxidized to form a metal oxide concurrent with the generation of electricity in the device. The anode may be oxidized by heating the device to any of the preferred operable temperatures disclosed herein when exposed to oxygen anions. Alternatively, the oxidized anode may be reduced by exposing the anode to a fuel, preferably at the temperatures disclosed herein.

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Current Collectors

In general, a current collector is any apparatus or portion thereof able to collect an electrical current, for example, from an electrochemical device such as a fuel cell, a battery, or an oxygen sensor. The term "collect," as used herein in reference to current collectors, does not necessarily imply a direction of current flow. Thus, a cathode current collector is exposed to a cathode, and an anode current collector is exposed to an anode. The cathode current collector may at least contact or otherwise maintain electronic communication with the cathode, and similarly the anode current collector may at least contact or otherwise maintain electronic communication the anode. In certain embodiments, the current collector may additionally be able to produce as well as collect electrical energy. In one embodiment, a current collector according to the present invention is capable of collecting an electrical output of at least about 10 mW/cm^2 , preferably at least about 50 mW/cm^2 , more preferably at least about 100 mW/cm^2 , more preferably at least about 200 mW/cm^2 , more preferably at least about 300 mW/cm^2 , and even more preferably at least about 500 mW/cm^2 . During current collection, the current

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collector may have an internal specific power loss of less than about 100 W/cm^2 , preferably less than about 1 W/cm^2 , more preferably less than about 10 mW/cm^2 , and still more preferably less than about $100 \text{ }\mu\text{W/cm}^2$, where the “specific power loss” may be defined as the amount of power lost per active area of the current collector while
5 current is being drawn through the current collector, for example, at a temperature of at least about $200 \text{ }^\circ\text{C}$. In other embodiments, the temperature may be at least about $300 \text{ }^\circ\text{C}$, about $500 \text{ }^\circ\text{C}$, about $800 \text{ }^\circ\text{C}$, about $1100 \text{ }^\circ\text{C}$, or higher. The active area is typically defined as the outer surface area of the current collector that is in contact with the anode.

As used herein, the terms “mixture,” “alloy,” or “compounds” refer to
10 compositions where two or more elements or materials are intermingled, for example, chemically, physically, or both.

Referring now to Fig. 12, in one embodiment of the invention, current collector 410 includes electrical connector 412 and electrically conducting core 414. The current collector may be positioned within electrode material 416. Electrical connector 412 may
15 be any connecting device that allows current collected from electrode material 416 to be transmitted. Electrically conducting core 414 may be made out of any material able to collect or transmit a current, and able to withstand the conditions of electrode material 416 during operation of the device. Electrode material 416 may be anodic or cathodic.

Electrically conducting core 414 may be constructed of any material or materials
20 able to collect or transmit a current. In some embodiments, the material of core 414 may be able to withstand exposure to the electrode material during operation; in other embodiments, the electrically conducting material may be surrounded by a sheathing material, and thus, may not be required to be able to withstand direct exposure to the electrode material. As used herein, a “sheathing material” is a material, auxiliary to the
25 electrically conducting material and to the electrode, that separates at least a portion of the electrically conducting material with at least a portion of the electrolyte and is able to withstand exposure to the electrode. That is, the sheathing material excludes oxide layers that may inherently occur on the electrically conducting material, for instance, when the electrically conducting material is in contact with air. “Able to withstand”
30 refers to materials that remain substantially unchanged, either chemically, physically, or structurally, upon exposure to the physical conditions of the electrode material for a sufficient time to provide a desired operating life. Examples of operating conditions, such as those involving a liquid anodic material, have been previously described. In

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some cases, the ability of a material to withstand an operating condition may be defined in terms of an erosion rate. The erosion rate may be defined to be the average rate of a decrease in the thickness of the material during a specific time frame. For example, in certain embodiments of the invention, the electrically conducting core, or a sheathing material, may have an erosion rate of less than about 5 cm per year, preferably less than about 1.8 cm per year, more preferably less than about 1 cm per year, or still more preferably, less than about 1 mm per year. In other embodiments, the electrically conducting core may include a metal, for example, a liquid metal.

In some cases, the electrically conducting material and/or the sheathing material may include a boride, such as TiB_2 , ZrB_2 , HfB_2 , TaB_2 , or NbB_2 . In other embodiments, the electrically conducting material and/or the sheathing material may include a carbide, such as TiC , TaC , ZrC , NbC , SiC , or WC , or the electrically conducting material and/or the sheathing material may comprise graphite. In other embodiments, the electrically conducting material and/or the sheathing material may include a nitride, such as ZrN , CrN , AlN , TiN , TiAlN , or TiCN . Combinations of these and other materials are also possible. In still other embodiments, the electrically conducting material and/or the sheathing material may include a metal, or a metal oxide. For example, the metal oxide may be an oxide of lanthanum, strontium, manganese, chromium, calcium, titanium, niobium, cerium, samarium, yttrium, gadolinium, indium, zirconium, scandium, or tin. In other cases, the metal oxide may include multiple metals, for example, a lanthanum-strontium-iron oxide, a lanthanum-strontium-chromium oxide, a lanthanum-calcium-chromium oxide, a lanthanum-strontium-titanium oxide, a strontium-titanium-niobium oxide, a cerium-niobium oxide, a cerium-samarium oxide, a cerium-yttrium oxide, or a cerium-gadolinium oxide. In still other embodiments, the electrically conducting material and/or the sheathing material may include a metal and/or a metal alloy, such as molybdenum, iron, tungsten, tantalum, ruthenium, nickel, copper, chromium, manganese, cobalt, titanium, scandium, steel, stainless steel, or a superalloy (e.g., HASTELLOY®, registered trademark of Union Carbide and Carbon Corporation Corp., New York, New York; INCONEL®, registered trademark of Inco Alloys International, Inc, Huntington, West Virginia). A superalloy is generally a high-temperature, high-strength alloy. For example, superalloys may be iron-based, nickel-based, or cobalt-based. Iron-based superalloys may be precipitation-hardened or precipitation-strengthened, and may include, for example, superalloy 16-25-6 (indicating its

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chromium, nickel, and molybdenum contents). Nickel-based superalloys may be oxide-dispersion strengthened or precipitation-hardened, and may include, for example, certain INCONEL® or HASTELLOY® alloys.

Other metals suitable for use in a current collector (e.g., in the electrically
5 conducting material and/or the sheathing material) may include noble metals, such as silver, gold, platinum, palladium, rhodium, osmium, or iridium. Combinations of the above compounds are also possible, such as alloys of any of the above metals, which may include combinations of the above metals or combinations with other metals as well. One example is a platinum-silver alloy having any suitable ratio, for example, 5%
10 Pt:95% Ag, 10% Pt:90% Ag, 20% Pt:80% Ag, or the like. In some embodiments, the electrically conducting material and/or the sheathing material may be a heterogeneous material formed from a mix of materials. The mixture may be a mixture including any one of the materials previously described, for example, a ceramic mixture, a metal mixture, or a cermet mixture, where a "cermet" is a mixture of at least one metal
15 compound and at least one ceramic compound, for example, as previously described. As one example, the cermet may include a material such as copper, silver, platinum, gold, nickel, iron, cobalt, tin, indium and a ceramic such as zirconium oxide, an aluminum oxide, an iron oxide, a nickel oxide, a lanthanum oxide, a calcium oxide, a chromium oxide, a silicate, a glass. Combinations of these materials are also contemplated.
20 Additionally, other materials may be incorporated in the cermet, for example, graphite. Suitable cermet mixtures may include, for example, Cu/YSZ, NiO/NiFe₂O₄, NiO/Fe₂O₃/Cu, Ni/YSZ, Fe/YSZ, Ni/LCC, Cu/YSZ, NiAl₂O₃, or Cu/Al₂O₃. As used herein, "LCC" refers to any lanthanum-calcium-chromium oxide.

The electrically conducting core may have any shape able to collect a current, for
25 example, a cylinder, a sphere, or a rectangular shape. The shape may be chosen as needed for a particular application, for example, due to space constraints, or to maximize or minimize the available surface area, for example, to maximize the contact area of the electrically conducting core with other components of the current collector or of electrode material 416. In some embodiments, the electrically conducting core may be
30 cylindrical, with a high aspect ratio, for example, so the core has a high surface area, or so that multiple cores may be easily packed together. Other core shapes are also possible.

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Electrical connector 412 may be any electrical connector able to transmit a current to or from the current collector. Electrical connector 412 may have any shape or size that may facilitate electrical connection. For example, electrical connector 412 may be a rod or a wire attached to or welded to the electrically conducting core, for example, as shown in Fig. 14. Electrical connector 412 may have any shape that may be used to attach electrical components to the current collector such that the electrical components are in electronic communication with the current collector. As used herein, "electronic communication" refers to any pathway which provides for the transport of electricity. For example, Fig. 19 shows a hooked electrical connector 412. In some embodiments, the electrical connection may be a copper wire. Electrical connector 412 may allow current to be carried to or away from the current collector. For example, electrical connector 412 may provide an electrical connection directly to an external load, or it may allow an electrical connection to a neighboring electrochemical device, such as in the case of a stack of electrochemical devices. In some embodiments, electrical connector 412 may be a low resistance connection that may, for example, minimize the voltage drop between the current collector and another device or connection.

Another embodiment of the invention is illustrated in Fig. 13, where current collector 410 includes an electrical connector 412, electrically conducting core 414, and sheathing material 418. Sheathing material 418 may have any shape able to surround or at least partially surround electrically conducting core 414, preferably a shape that prevents external material from entering the current collector. For example, the shape of sheathing material 418 may be cylindrical with one or two sealed ends. Sheathing material 418 may also be spherical or rectangular. The design of sheathing material 418, in some embodiments, may be a function of the shape of the electrically conducting core. In other embodiments, the design and shape of sheathing material 418 may be chosen for other reasons, for example, to minimize the contact area of the current collector with electrode material 416, which may minimize long term degradation of the current collector over extended periods of time, or to maximize the contact area of the current collector with electrode material 416, which may maximize the ability of the current collector to collect a current.

In some embodiments, sheathing material 418 may be any material able to, for example, withstand the conditions of electrode material 416 during operation, or withstand the environment that the electrode material is in. In some cases, sheathing

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material 418 may also be electrically conductive, or sheathing material 418 may include a surface coating or plating by a material that improves its electrical conductivity (for example, such that the sheathing material has a conductivity of at least about 0.001 S/cm in some embodiments, at least about 0.01 S/cm in other embodiments, at least about 0.1 S/cm in still other embodiments, at least about 1 S/cm in still other embodiments, at least about 10 S/cm in still other embodiments, or at least about 100 S/cm in still other embodiments). The conductivity may be a function of the material or materials used to construct the sheathing material or the coating thereon, or it may be due to the presence of pores or other “defects” within the material that allow the passage of current across sheathing material 418, for example, electrical or ionic current. In this embodiment, electrically conducting core 414 is not necessarily required to be able to withstand the operating conditions of electrode material 416, as it is protected by sheathing material 418 and is not directly exposed to electrode material 416. In certain embodiments, the material at least partially coated or plated onto the sheathing material may stabilize or improve electrical contact within the current collector, for example, between sheathing material 418 and any internal components such as electrically conducting core 414, or with external components such as electrode material 416. Any material able to improve the conductivity of sheathing material 418 may be used as a coating, for example, an electroplatable metal such as nickel or copper. Other suitable sheathing materials may include, for example, gold, platinum, silver, rhodium, rhenium, osmium, palladium, as well as combinations of these materials.

In still other embodiments, the design, composition, coating material, or the shape of sheathing material 418 may be chosen due to other considerations, for example, to contain a liquid inner material within the current collector or to allow or inhibit gas exchange. As used herein, “substantially solid” generally refers to devices where the device maintains its external shape at temperatures that the device is designed to operate at, for example, a temperature of greater than about 200 °C, greater than about 300 °C, greater than about 500 °C, greater than about 750 °C, or greater than about 1000 °C. While the current collector may remain substantially solid at its operating temperatures, internal components of the current collector may stay solid, become liquid, or mix with certain other components during operation. For example, an inner material located within the sheathing material 418, may become a liquid at the operating temperature of

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the current collector. However, as the sheathing material 418 remains solid, the current collector is able to remain substantially solid.

In Fig. 13, for example, sheathing material 418 may prevent electrode material 416 from contacting electrically conducting core 414. In this embodiment, electrically
5 conducting core 414 may not be able to withstand direct exposure to electrode material 416, but due to the presence of sheathing material 418, is not directly exposed to electrode material 416. In other embodiments, sheathing material 418 may surround a portion of electrically conducting core 414, but still allow a limited amount of direct contact between electrically conducting core 414 and electrode material 416. Thus,
10 sheathing material 18 is able to limit or prevent contact between electrode material 416 and electrically conducting core 414, thus inhibiting reaction between the electrode material and the core.

Sheathing material 418 may have any thickness that, for example, allows migration of ions or other species across the sheathing material, or allows transport of
15 oxygen or other gases to or from electrically conducting core 414, or any other materials inside the current collector. The thickness may be chosen, for example, to ensure adequate separation of the internal components of the current collector from the electrode material, while allowing reliable transport of species or minimizing cost. For example, in some embodiments the thickness of sheathing material 418 may be less than about 500
20 μm , less than about 300 μm , less than about 200 μm , or less than about 100 μm . A smaller thickness, for example, less than about 50 μm or less than about 10 μm , may provide for more efficient migration of ions, transport of oxygen or other gases across the material, or facilitate the design of miniaturized devices.

Sheathing material 418 may be constructed from one or more materials able to
25 withstand the physical operating conditions of the electrode material, as previously described. For example, the operating conditions may include temperatures between about 200 °C and about 2500 °C, or about 300 °C and about 2500 °C. Examples of materials that may be used to construct sheathing material 418 include a metal oxide or a mixed metal oxide. Specific examples include tin-doped In_2O_3 , aluminum-doped zinc
30 oxide and zirconium-doped zinc oxide. In other cases, the metal oxide may be a lanthanum-calcium-chromium oxide, a cerium-niobium oxide, a cerium-gadolinium oxide, a cerium-oxide-samarium oxide, a cerium oxide-yttrium oxide, or a strontium-titanium-niobium oxide. Another example is a perovskite-type oxide having a general

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structure of ABO_3 , where "A" and "B" represent two cation sites in a cubic crystal lattice. A specific example of a perovskite-type oxide has a structure $La_xMn_yA_bB_cO_d$ where A is an alkaline earth metal, B is selected from the group consisting of scandium, yttrium and a lanthanide metal, C is selected from the group consisting of titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, hafnium, aluminum and antimony, x is from 0 to about 1.05, y is from 0 to about 1, a is from 0 to about 0.5, b is from 0 to about 0.5, c is from 0 to about 0.5 and d is between about 1 and about 5, and at least one of x, y, a, b and c is greater than zero. More specific examples of perovskite-type oxides include $LaMnO_3$, $La_{0.84}Sr_{0.16}MnO_3$, $La_{0.84}Ca_{0.16}MnO_3$, $La_{0.84}Ba_{0.16}MnO_3$, $La_{0.65}Sr_{0.35}Mn_{0.8}Co_{0.2}O_3$, $La_{0.79}Sr_{0.16}Mn_{0.85}Co_{0.15}O_3$, $La_{0.84}Sr_{0.16}Mn_{0.8}Ni_{0.2}O_3$, $La_{0.84}Sr_{0.16}Mn_{0.8}Fe_{0.2}O_3$, $La_{0.84}Sr_{0.16}Mn_{0.8}Ce_{0.2}O_3$, $La_{0.84}Sr_{0.16}Mn_{0.8}Mg_{0.2}O_3$, $La_{0.6}Sr_{0.35}Mn_{0.8}Al_{0.2}O_3$, $La_{0.84}Sc_{0.16}MnO_3$, $La_{0.84}Y_{0.16}MnO_3$, $La_{0.7}Sr_{0.3}CoO_3$, $LaCoO_3$, $La_{0.7}Sr_{0.3}FeO_3$, and $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$. It is to be noted that the elements forming the sheathing material do not necessarily have to be present in a fixed stoichiometric integer ratio, as illustrated by the above examples.

Other examples of materials that may be suitable for constructing at least a part of sheathing material 418 include oxides such as lanthanum-calcium-chromium oxide, a lanthanum-strontium-chromium, a lanthanum-strontium-manganese oxide, an indium-tin oxide, a lanthanum oxide, a strontium oxide, a calcium oxide, an iron oxide, a cobalt oxide, a manganese oxide, a magnesium oxide, a titanium oxide, as well as mixtures of these. Specific non-limiting examples may include $LaCoO_3$, $LaFeO_3$, $LaCrO_3$, or a $LaMnO_3$ -based perovskite oxide material, such as $La_{0.75}Sr_{0.25}CrO_3$, $(La_{0.6}Sr_{0.4})_{0.9}CrO_3$, $La_{0.6}Sr_{0.4}FeO_3$, $La_{0.6}Sr_{0.4}CoO_3$ or $Ln_{0.6}Sr_{0.4}CoO_3$, where Ln ("lanthanide") may be any lanthanide found in the Periodic Table, and preferably, one of lanthanum, praseodymium, neodymium, samarium or gadolinium. In other embodiments, sheathing material 418 may comprise zirconia or other zirconium compounds.

Alternatively, sheathing material 418 may comprise a metal. Example metals include platinum, palladium, molybdenum, lead, iridium, indium, nickel, iron, gold, silver, copper, rhodium, chromium, and combinations thereof.

Any method may be used to apply or form sheathing material 418, or a coating or plating layer thereon. For example, standard thin film processing may be used. Examples of thin film processing techniques include, but are not limited to, chemical vapor deposition, physical vapor deposition, electron bombardment, painting,

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electroplating, ion implantation, sputtering, thermo-spraying, dip coating, doping, being synthesized directly *in situ*, or the like. Plasma spray methods may be preferred in certain embodiments, where the material to be applied is heated (for example, as a powder). The material is then sprayed directly onto a surface, which may, for example, eliminate the need to separately heat the surface, or eliminate the need to cure or sinter the applied material.

In some embodiments of the invention, sheathing material 418 is formed of a material that allows the migration of ions between electrode material 416 and inner portions of the current collector. In other embodiments, the material itself may be able to pass ions or electrons; in still other embodiments, however, the material may be electrically or ionically insulating, but the material may have pores, channels or other “defects” that may allow the passage of ions or electrons across the material. In other embodiments, sheathing material 418 may be insulating and defect-free, but may not fully surround electrically conducting core 414.

In certain embodiments of the invention, additional materials may be present within the current collector. These materials may be located, for example, between sheathing material 418 and electrically conducting core 414. The material may have any shape or configuration and may be positioned anywhere between sheathing material 418 and electrically conducting core 414. For example, in one embodiment, the material may have two layers, one layer which may provide mechanical stiffness to the current collector, and another layer which may provide at least partial erosion protection, corrosion protection, or any other form of chemical or mechanical protection for the current collector. As another example, the material may provide several functions for the current collector, for example, a combination of mechanical toughness and corrosion protection. The additional materials may conform to the shapes of sheathing material 418 and electrically conducting core 414, or the materials may be in deformable contact with the sheathing material, the electrically conducting core, or each other, depending on the specific application.

For example, in the embodiment of the invention shown in Fig. 14, current collector 410 may include electrical connection 412, electrically conducting core 414, and sheathing material 418. The current collector may also include inner material 420, joint 422, and vent 424. Inner material 420 may be any material that allows the passage of current from electrode material 416 to electrically conducting core 414, for example, a

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ceramic or a liquid metal. Joint 422 may connect sheathing material 418 and vent 424, and may have any shape able to protect at least a part of the inner portions of the current collector from electrode material 416, for example, a shield, a tube, or a baffle. As one example, if electrode material 416 comprises a liquid, then joint 422 may prevent “tin splash,” or the splashing of liquid tin from electrode material 416 from entering current collector 410. Joint 422 may be constructed out of any material able to at least partially withstand the conditions of the electrode material during operation, for example, a metal, or a ceramic such as alumina or aluminum oxide, a silicate, or a zirconium oxide. Combinations of materials (e.g., as in a cermet) are also contemplated.

10 Another example involving a different configuration is illustrated in Fig. 24. In this embodiment, current collector 410 is positioned along one side of electrode material 416. As another example, in the embodiment shown in Fig. 28, an electrically conducting core material 570, such as stainless steel, may be surrounded by a sheathing material 580, such as platinum. In some cases, the sheathing material may be thick enough to be able to prevent degradation of electrically conducting core material 570, while being thin enough to reduce costs. In certain cases, between electrically conducting core material 570 and sheathing material 580 is inner material 575. Inner material 575 may conform to either or both of core material 570 or sheathing material 580, or inner material 575 may be in deformable contact with one or the other.

20 An external agent may be delivered to the electrochemical device that interacts with current collector 410 in certain embodiments, e.g., the agent may be delivered directly into or immediately outside of current collector 410. The external agent may be, for example, a liquid or a gas, a fuel, an inert agent (relative to the current collector), or the like. In some embodiments, the external agent may be used to maintain favorable operating conditions around or within the current collector. For example, the external agent may be a non-oxidizing agent able to inhibit (i.e., reduce or eliminate) the amount of oxidation that occurs in the current collector. As another example, the current collector may internally require an oxidizing or reducing environment for operation that is different from the environment surrounding the current collector. The environment needed by the current collector for operation may be contained specifically within the current collector, or the environment may surround the current collector, for example, an environment maintained by a container around the current collector. As yet another example, the interior of current collector 410 may include a reaction by-product (for

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example, one that interferes with device operation) that may be neutralized or displaced by a suitable external agent.

As one example, current collector 410 may be susceptible to having a passivating layer that forms on its surface when the current collector is exposed to a reducing or an oxidizing environment. The formation of a passivating layer on current collector 410 may, in some cases, protect the interior of the current collector from undergoing further oxidation or corrosion. In some cases, the formation of a passivating layer allows a material unable to withstand the oxidizing or reducing environment to be used in current collector 410, due to the protective effects of the passivating layer. The formation of a passivating layer may also increase the electrical resistance of current collector 410. In some embodiments, the formation of a passivating layer sufficiently thick to prevent further oxidation of current collector 410 while being reasonably thin to minimize electrical resistance may be useful. In one particular example, the exterior of a current collector may comprise chromium, and exposure to an oxidizing environment causes the surface of the chromium to oxidize to form a passivating layer thereon, which may contain, for example, a form of chromium oxide. In one embodiment, the reducing environment has an oxygen partial pressure of less than about 0.0001 atm, and in other embodiments the oxygen partial pressure may be less than about 0.00001 atm or less than about 0.000001 atm.

The application of an external agent to current collector 410 may substantially reduce the thickness of the passivating layer that forms on the current collector, or prevent the formation or growth of the passivating layer. For instance, in the example given above, the application of an external agent such as hydrogen gas or methane to the current collector may substantially reduce the thickness of the chromium oxide layer.

In one embodiment, the external agent applied to current collector 410 may be a gas. The gas may be a gas that is inert or unreactive towards the current collector, for example, a noble gas such as helium or argon, or the gas may be a reducing gas, i.e., a gas able to reduce another species, such as hydrogen, carbon monoxide, a hydrocarbon (for example, methane), or the like. In some cases, the internal reducing environment has an oxygen partial pressure of less than about 0.0001 atm, less than about 0.00001 atm, or less than about 0.000001 atm. Other reducing agents are known by those of ordinary skill in the art. In another embodiment, the external agent may comprise a fuel, for example, fuel that is supplied to the electrical device, or another fuel, such as a

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carbonaceous material. As one example, fuel that is supplied to the device may not fully react within the electrochemical device. Unreacted or exhaust fuel from the device may then be applied to the current collector, for example, to minimize the thickness of, or eliminate the passivating layer in some cases. In some cases, the exposure of fuel or
5 other external agents to the current collector may slightly reduce the amount of energy that the device can produce, as the fuel shunted to the current collector may, for example, chemically react with the passivating layer, or, in cases where the fuel is introduced into the cathode, the fuel may be directly oxidized without producing an electrochemical current.

10 Vent 424 allows fluids to flow to or from the current collector. For example, a gas such as oxygen or carbon dioxide may be produced or consumed by the device during operation and may flow through vent 424; or a reducing agent or fuel may be delivered to or from the device. Vent 424 may be located anywhere within the device and may be constructed in any manner that allows fluids to flow into or out of the device.
15 For example, vent 424 may be located adjacent to inner material 420, or electrically conducting core 414. For example, as illustrated in Fig. 14, vent 424 allows fluids such as gases generated by electrically conducting core 414 or inner material 420 to escape, for example, during electrochemical reaction and production of electrical current. In other embodiments of the invention, gases, liquids, fuels, and the like may be introduced
20 through vent 424. The vent may be in fluid communication with the electrically conducting core, or with any of the internal materials. In certain embodiments, the vent may be a cylindrical tube, or be an open outlet at the top of the current collector. Vent 424 may be constructed out of any material able to at least partially withstand the conditions of the liquid electrode material during operation. Typical operation
25 conditions that may be encountered have been previously described above. In some cases, the material used to form vent 424 may have a high melting point, preferably greater than the melting point of the electrode material. For example, in one embodiment, the structure may be constructed out of alumina. In other embodiments, any of the materials previously described may be used in the construction of the vent.
30 The material for the vent may also be made out of an electrolyte material, zirconia, a glue such as a porous glue, or from a porous ceramic, for example, porous alumina, porous zirconia, or any other porous electrolyte.

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In some embodiments of the invention, joint 422 may be used to connect vent 424 and sheathing material 418. Joint 422 may be constructed out of any material able to at least partially withstand the conditions of the liquid electrode material during operation. Typical operating conditions that may be encountered have been described previously. In some cases, the material used to form joint 422 may have a high melting point, preferably greater than the melting point of the electrode material. For example, joint 422 may be formed out of a glue having a high melting point, such as an alumina glue. Other suitable materials may include zirconia or oxide materials. For example, the glue may comprise pure alumina, a commercially available material such as Cotronics 552 (available from Cotronics Corp., Brooklyn, NY), zirconia material that is sintered at high temperature to form a bond. The glue used in joint 422 may also contain binders, for example, that allow the material to be cured in an oven. In some embodiments, the glue may have some mechanical strength. The glue may or may not be porous enough to allow air or exhaust to pass through it, depending on the application.

In certain embodiments, joint 422 may also be able to prevent electrode material from entering the current collector. For example, in Fig. 14, joint 422 surrounds a portion of electrically conducting core 414, as well as sheathing material 418 and inner material 420. Joint 422 may have any shape and thickness able to keep material from entering into the current collector, for example, a cylindrical shield, a ring-like structure or a series of baffles.

Sheathing material 418 in Fig. 14 may prevent electrode material 416 from contacting either electrically conducting core 414, or inner material 420. For example, if the inner material comprises a liquid, then inner material 420 will not be exposed to, and will not mix with, electrode material 416. Additionally, electrically conducting core 414, which may not be able to withstand direct exposure to electrode material 416, may be prevented from being affected by electrode material 416. For example, the sheathing material may be designed for corrosion, erosion, or degradation protection, while the electrically conducting core may principally be a suitable electrical conductor.

The inner material or materials may be any materials suitable to be positioned within the current collector. Examples of materials include the materials previously described for the sheathing material or the electrically conducting core. In some embodiments, one or more of the internal materials may include a metal. In some cases, this metal may be in liquid form during operation of the current collector. Examples of

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metals that may be used in the inner layer include copper, molybdenum, iridium, palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, chromium, nickel, iron, tungsten, cobalt, zinc, vanadium, gallium, or aluminum, as well as alloys of these metals. As a specific example, the current collector may be composed of an inner molybdenum alloy rod, an outer YSZ sheathing material, and a liquid metal middle layer connecting the sheathing material with the electrically conducting core.

In certain cases, internal material 420 may be either a liquid or a solid, depending on the operating conditions of the current collector, or the number of times that the current collector has been used. As one specific example, in a current collector comprising nickel and tin, the current collector may be constructed such that the nickel and tin initially are separate components within the current collector. The operating temperature of the current collector may be a temperature such that pure tin would be a liquid and pure nickel would be a solid, while an alloy of nickel and tin would also be a solid. Thus, upon initial heating of this current collector during use, the tin may melt to form a liquid once the melting point of tin has been reached. The molten tin may mix or alloy with nickel to form a nickel-tin alloy, which is a solid at the operating temperature. The current collector may satisfactorily continue to collect current during operation, even though the internal arrangement of the current collector may change over time,

One embodiment of the invention, as used in an electrochemical device such as a solid oxide fuel cell, is illustrated in Fig. 15. In Fig. 15, current collector 410 includes electrical connection 412, electrically conducting core 414, and sheathing material 418. Current collector 410 is positioned in contact with electrode material 416 in this embodiment. Electrode material 416 is contained within an electrically conducting container 436, in electronic communication with electrolyte 438. Electrolyte 438, which may be a solid or a liquid, may be in electronic communication with cathode current collector 440 and electrical connector 442. An example use of Fig. 15 is as follows: a fuel is introduced into electrode material 416, where it is oxidized to produce current that is collected by current collector 410. Electrical connectors 412 and 442 may be connected to any external electrical device that uses or stores energy, such as a battery or a circuit. Under certain operating conditions, either or both of inner material 420 and electrode material 416 may comprise a liquid metal.

More than one sheathing material may also be present within the current collector. Example representations of various geometries are illustrated in Figs. 16-18. In one set of embodiments, two outer layers of material 426, 428 may be present, as illustrated in Fig. 16. In other embodiments, three layers (426, 428 and 430 in Fig. 17),
5 or more than three layers (434 in Fig. 18) may be present, all surrounding at least a portion of the electrically conducting core. Other configurations, involving multiple sheathing materials, or multiple inner liquid materials, can be envisioned by those of ordinary skill in the art. For example, one layer of material may be a corrosion resistant layer (i.e., a layer that does not corrode during operation of the current collector), while
10 another layer may provide good electrical conduction, or provide thermal insulation. The materials may be able to maintain their desired properties during operation without needing frequent replacement. As one example, in the embodiment illustrated in Fig. 16, layer 426 may be a corrosion resistant layer of material that prevents electrode material 416 from contacting electrically conducting core 414. Layer 428, positioned between
15 layer 426 and electrically conducting core 414 may provide better electrical contact between electrically conducting core 414 and layer 426, or it may, in some cases, be a second layer of corrosion resistant material, for example, it may be resistant against species able to diffuse or migrate through layer 426. Other configurations may also be possible, depending on the desired function of the surrounding layers of material, such as
20 previously described with sheathing material 418. The actual configuration of sheathing and internal materials will be a function of the specific application of the device.

The current collector may be in direct or conforming contact with the electrode material, or the current collector may be in deformable contact with the electrode material, for example, by using an appropriately-shaped current collector, or in cases
25 where the electrode material is liquid. Several examples are illustrated in Figs. 12 and 20-23. Fig. 12 shows current collector 410 in deformable contact with electrode material 416. Electrode material 416 may be, for example, a liquid or a viscoelastic solid. In Fig. 20, current collector 510, having a series of bristles 530, is in deformable contact with electrode material 520. Although not all of bristles 530 directly contact electrode
30 material 520, enough of the bristles do such that electrical communication may be maintained between current collector 510 and electrode material 520. In Fig. 21, electrode material 520 and current collector 510 maintain deformable contact via fluid 540, which may be, for example, a liquid, a viscoelastic solid, a gel, or the like. In Fig.

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22, current collector 555 is formed from a series of interwoven wires 560, which may be, for example, fashioned as a braid of wires. The wires may be fashioned out of any conducting material, for example, stainless steel, speaker wire, copper wire, oxygen-free copper wire, silver wire, gold wire, nickel wire, or OFHC (“oxygen-free high-
5 conductivity”) wire. The wires may also be plated with a coating material in some cases, for example, with gold, silver, or nickel, which may, for example, improve corrosion resistance, improve conductivity, or improve external contact or adhesion. Combinations of these wires and other wires may also be envisioned. The wire may be a single strand, or be formed of multiple strands, for example, as in finely stranded cable or course
10 stranded cable. Similar to the situation depicted in Fig. 20, enough of wires 560 of current collector 555 are able to maintain contact with electrode material 520 to maintain electronic communication between electrode material 520 and current collector 555. In Fig. 23, material 550 maintains electronic communication between current collector 510 and electrode 520. Material 550 may have any shape or conformation suitable for
15 maintaining communication, for example, if the shape of either or both of current collector 510 and electrode material 520 changes, for example, due to changes in temperature. Suitable shapes of material 550 include, but are not limited to, a felt, a fabric, a corrugated shape, or the like. Other methods of maintaining deformable contact between current collector 510 and electrode 520 are also contemplated, and are not
20 limited to the figures described herein.

It should be understood that the embodiments described herein are example and non-limiting. Consequently, the system as illustrated in the figures may be modified as needed for a particular process. For example, additional or multiple sheathing materials may be added around the electrically conducting core, multiple electrically conducting
25 cores may be used, or additional electrical connections and components may be added without departing from the scope of the invention.

It is to be understood that a variety of configurations may exist in the present invention. For example, the current collector may include additional elements to allow it to be positioned within an anode or within an electrical device, or the current collector
30 may be an integral part of a larger electrochemical apparatus. In some cases, systems of the invention may include additional components than those illustrated; and, in some cases, systems of the invention may not include all of the illustrated components.

Current Collectors Exposed to Anodic Material

In one set of embodiments, the current collector may be placed in contact with any anodic material to construct an electrode suitable for use in an electrochemical device, for example, as described in U.S. Patent Application Serial No. 09/033,923, filed
5 March 3, 1998, entitled "A Carbon-Oxygen Fuel Cell"; U.S. Patent Application Serial No. 09/837,864, filed April 18, 2001, entitled "Electrochemical Device and Methods for Energy Conversion"; or U.S. Patent Application Serial No. 09/819,886, filed March 28, 2001, entitled "Carbon-Oxygen Fuel Cell"; all of which are incorporated herein by reference in their entirety. For example, the electrode may be the anode electrode of an
10 electrochemical cell. As used herein, "anodic material" refers to any material capable of functioning as an anode in, for example, a fuel cell, such as a solid oxide fuel cell, or a battery. Examples of anodic material include metals such as main group metals, transition metals, lanthanides, or actinides. Other examples include ceramics or doped ceramics. Examples of ceramics include cerium oxide (CeO_2), indium oxide (In_2O_3), tin
15 oxide, vanadium carbide and vanadium oxide (V_2O_5). The ceramic may include more than one type of metal ion. Examples include copper/cerium oxides or tin/indium oxides. In some embodiments, the dopant metal (i.e. the metal ion doped in the oxide) may be present in an amount ranging from trace amounts to about 50 mol%. In other embodiments, the dopant metal may be present in an amount from about 2 mol% to
20 about 50 mol%, from about 10 mol% to about 40 mol%, or from about 20 mol% to about 30 mol%. Examples include cerium doped YSZ, nickel in YSZ, gadolinium doped cerium oxides and samarium doped cerium oxides. "YSZ," as used herein, refers to any yttria-stabilized zirconia material, for example, $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$.

In embodiments where the anodic material comprises a metal, the metal may be a
25 pure metal, or it may be an alloy comprising two or more metals. Any portion of the anodic material that is oxidized may form a metal oxide. A mixed metal oxide may be formed in the case where the anode is an alloy. In some embodiments, the metal has a standard reduction potential greater than -0.70 V versus the Standard Hydrogen Electrode (determined at room temperature). These values can be obtained from
30 standard reference materials or measured by using methods known to those of ordinary skill in the art. In another embodiment, where the anode comprises more than one metal, all metals preferably may have a standard reduction potential greater than -0.70 V versus the Standard Hydrogen Electrode. Balancing the various electrochemical potential

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requirements can be determined by those of ordinary skill in the art. In certain embodiments, an alloy may be used where at least one of the metals does not have a standard reduction potential greater than -0.70 V, but is included in the alloy to enhance flow properties, consistency, or other properties not related to electrochemical potential.

5 In other embodiments, the anode may comprise a mixture of a metal and a non-metal to enhance flow properties, consistency, or other properties not related to electrochemical potential.

The metal within the anodic material may comprise a metal or alloy including at least one of a transition metal, a main group metal, an alkaline metal, an alkaline earth

10 metal, a lanthanide, an actinide and combinations thereof. In another embodiment, the anodic material may comprise a material such as copper, molybdenum, mercury, iridium, palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, gadolinium, chromium nickel, iron, tungsten, cobalt, zinc, vanadium or combinations thereof. For

15 example, the anode may include a pure metal such as antimony, indium, tin, bismuth, mercury and lead. In another embodiment, the anode may include an alloy of at least one element such as copper, molybdenum, mercury, iridium, palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, gadolinium, chromium, nickel, iron,

20 tungsten, vanadium, manganese, cobalt, zinc and combinations thereof. Examples of alloys include 5% lead with the remainder antimony, 5% platinum with the remainder antimony, or 5% copper with the remainder indium. Other alloys may further include various percentages of different metals with the alloys; for example, the alloys may include 20% lead, 10% silver, 40% indium, or 5% copper within the alloy in different

25 embodiments.

In other embodiments, the anodic material may include other non-metal components, for example, a conducting ceramic, preferably one that is molten at any of the operating temperatures disclosed herein.

In certain embodiments, the current collectors of the present invention may be

30 used in liquid anode environments, i.e., the anodic material (for example, any of the materials previously described) may be a pure liquid or may have solid and liquid components, so long as the anodic material as a whole exhibits liquid-like properties. A liquid is a material that exhibits flow properties. In some embodiments, a liquid is a

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material which exhibits a tendency to flow in response to an applied force under given operating conditions of temperature and pressure. Liquids generally have little or no tendency to spontaneously disperse. Preferably, materials that flow within a time scale that is not perceptible to humans are generally excluded from this definition.

5 One advantageous feature of a liquid anode in certain embodiments involves the ability of the anode to act as a sealant precursor to seal a flaw in a solid component of the current collector. For example, when a portion of the current collector develops a crack or other flaw, the liquid metal anode may flow to substantially cover and/or substantially fill the crack. Subsequently, the anode may react with oxygen to form a metal oxide (or
10 mixed metal oxide in the case where the anode is an alloy). The resulting oxide formed substantially conforms to the crack due to the flow properties of the initially liquid anode. Even though the present invention is able to minimize thermal and mechanical stresses, the repair capability of the anodic material may help to ensure the integrity of the invention, particularly when repair is not feasible, e.g. during operation of the
15 system.

 Another aspect of the invention may be used in embodiments wherein the anode is a chemically rechargeable anode. A "chemically rechargeable anode" refers to an anode capable of being recharged by the addition of a chemical reductant, as opposed to conventional electrically rechargeable devices. Ideally, during recharging of the anodic
20 material, the current collector does not react with the chemical reductant. The presence of the chemical reductant may prevent the anodic material itself from being oxidized. During certain modes of operation of the electrochemical device, at least a portion of the anode may be consumed with the release of electrons. A "consumed" anode or portion of the anode refers to an anode having a higher oxidation state than the initial oxidation
25 state, i.e., the anode is oxidized. Chemical recharging may be initiated by exposing the portion of the consumed anode to a chemical reductant resulting in that portion being reduced to a more reduced state, such as the initial oxidation state. Thus, it is the chemical reductant, not electricity that, at least in part, recharges the anode. In one embodiment, the chemical reductant alone causes recharging of the anode. In another
30 embodiment, a combination of chemical and electrical recharging results in restoration of the anode. An advantage of chemical recharging is the provision that the recharging species (i.e., the chemical) are located within the anodic material itself. Thus, no recharging species external to the anodic material may be needed. In another

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embodiment, the chemical reductant may be the fuel itself. The fuel may chemically recharge or reduce the oxidized anode to its initial state via a chemical reaction, where a portion of the fuel reduces the anode and another portion of the fuel is oxidized to generate electricity. In other embodiments, however, it may be desired to incorporate
5 another chemical reductant specifically for recharging the anode.

In one set of embodiments, the current collector may be configured to allow recharging with electricity, for example, in addition to a chemical recharging capability. Certain anodic materials and certain fuel types may also be recharged electrically. For some applications, it is preferred that the current collector is able to function in
10 environments where the anodic material is both chemically and electrically rechargeable.

In one embodiment, the current collector is operable, with the anodic material surrounding the current collector in a liquid state, at a temperature of less than about 1500 °C, preferably at a temperature of less than about 1300 °C, more preferably less than about 1200 °C, even more preferably less than about 1000 °C, and even more
15 preferably less than about 800 °C. By "operable," it is meant that the current collector is able to collect electricity, either during operation of the electrochemical device with production of electricity, or during recharging of the anodic material, for example, chemically or electrically. The anodic material may not necessarily be a liquid at room temperature. It is understood by those of ordinary skill in the art that the anodic
20 temperature may be controlled by selection of anode materials or in the case of an alloy, composition and percentages of the respective metal components, i.e., composition may affect a melting point of the anode. Other example operating temperature ranges where the current collector may be designed to be operable at include, but are not limited to, a temperature between about 200 °C to about 1500 °C, between about 300 °C to about 1500
25 °C, between about 500 °C to about 1300 °C, between about 500 °C to about 1200 °C, between about 500 °C to about 1000 °C, between about 600 °C to about 1000 °C, between about 700 °C to about 1000 °C, between about 800 °C to about 1000 °C, between about 500 °C to about 900 °C, between about 500 °C to about 800 °C, and between about 600 °C to about 800 °C. Other embodiments may include other
30 temperature ranges. For example, the temperature range may be between about 1000 °C to about 1500 °C, between about 1500 °C to about 2000 °C, between about 2000 °C to about 2500 °C, between about 700°C to about 1300°C, between about 1200°C to about

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1800°C, between about 1700°C to about 2300°, between about 1400°C to about 1700°C, or between about 300°C to about 2500°C.

Another advantageous feature of a liquid anode is that by positioning a liquid adjacent to a solid component of the current collector, a non-permanent seal may be formed. This non-permanent attachment removes a need to add further components to hold each device adjacent to the other, for example, by use of adhesives or mechanical attachments. In the event of a malfunction of the current collector, the malfunctioning current collector may be removed and easily replaced with a new device. Of course, other embodiments may provide a permanent seal in addition, depending on the application.

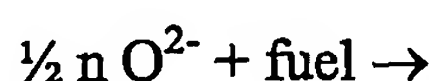
In one embodiment, the current collector is operable at a temperature at which any of the solid state components are not easily susceptible to cracking, i.e., the solid state components preferably maintain their structural integrity at the operating temperature of the device. In another embodiment, the current collector is operable at a temperature at which the anode does not react with any of the solid state components. In another embodiment, the current collector is operable at a temperature at which the anodic material comprises a liquid. One or any combination of these embodiments may be practiced independently or in combination, and those of ordinary skill in the art can balance these embodiments with the knowledge that increasing operational temperatures generally result in an increase in electrical output.

In one set of embodiments, the current collector may collect electrons from a reaction of a metal with oxygen anions, as shown in Eq. 5:



In this equation, M represents a metal, and n and x are each greater than or equal to 0. Electrons from this reaction may be collected by the current collector into a resultant current.

Additionally, in the presence of fuel, a variety of reactions may occur. The fuel may be oxidized at the anode, thereby releasing electrons to be collected by the current collector, as represented in Eq. 6:





Eq. 2 is intended to represent some of the various possible oxidation products. The coefficients a, b, c, d, x, y, and z may be the same or different and each are greater than or equal to zero and their values depend on the type of fuel used, and at least one of a, b, c, d, x, y, and z will be greater than zero. For example, CO_x may represent CO_2 , CO or a mixture thereof. The coefficient "n" may be greater than 0. The fuel may comprise any combination of "a" carbon atoms and/or "b" nitrogen atoms and/or "c" sulfur atoms and/or "d" hydrogen atoms, etc. For example, if hydrogen is the fuel, water is the sole oxidation product. Not all possible oxidation products are represented by Eq. 2 and depending on the composition of the fuel, those of ordinary skill in the art can determine the resulting oxidation product.

Examples of fuels include a carbonaceous material; biomaterials such as cellulose or protein; sulfur; a sulfur-containing organic compound such as thiophene, thiourea and thiophenol; a nitrogen-containing organic compound such as nylon and a protein; ammonia, hydrogen and mixtures thereof. Examples of a fuel comprising a carbonaceous material include conductive carbon, graphite, quasi-graphite, coal, coke, charcoal, fullerene, buckminsterfullerene, carbon black, activated carbon, decolorizing carbon, a hydrocarbon, an oxygen-containing hydrocarbon, carbon monoxide, fats, oils, a wood product, a biomass and combinations thereof. Examples of a hydrocarbon fuel include saturated and unsaturated hydrocarbons, aliphatics, alicyclics, aromatics, and mixtures thereof. Other examples of a hydrocarbon fuel include gasoline, diesel, kerosene, methane, propane, butane, natural gas and mixtures thereof. Examples of oxygen-containing hydrocarbon fuels include alcohols which further include C_1 - C_{20} alcohols and combinations thereof. Specific examples include methanol, ethanol, propanol, isopropanol, cyclopropanol, propenol, butanol and mixtures thereof. However, almost all oxygen-containing hydrocarbon fuels capable of being oxidized by the anode materials disclosed herein. Gaseous fuels such as hydrogen and SynGas (a mixture of hydrogen and carbon monoxide) may also be used in certain embodiments of the invention.

One advantageous feature of a liquid anode is that fuel may be dispersed throughout the anode regardless of the physical state of the fuel, i.e., a gaseous, liquid or solid fuel may be dispersed throughout the anode. The electrical output may be

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increased by increasing the surface area of an anode. Dispersing fuel throughout the anode may allow maximization of the surface area exposed to the fuel. In addition, the liquid may be agitated by stirring or bubbling (or any other agitation methods) to help disperse the fuel throughout the liquid.

5 In another aspect of the invention, the current collector may be capable of operating with more than one type of fuel present in the anodic material. This aspect of the invention makes it possible to capitalize on the benefits of different fuel types. For example, in one embodiment, one fuel type may be used to provide a higher power output, and a second type of fuel may be added that provides a lower power output but is
10 lighter in weight. In another embodiment, enhanced performance may be achieved with one type of fuel, while another type of fuel may recharge the anodic material more efficiently. Other benefits for using different types of fuel may be realized, for example, in situations where cheaper fuel is required, or where environmental concerns dictate the choice of fuel. In some cases, the anodic material may include more than one type of
15 fuel.

Current Collectors Exposed to Cathodic Material

As described above, the cathode ionizes oxygen to oxygen ions as represented by the electrochemical half reaction shown in Eq. 7:

20



The cathode and the cathode current collector may be exposed to any oxidizing agent during operation, such as air, pure oxygen or an oxygen-containing gas, at atmospheric
25 pressures or greater. Oxygen may be reduced at the interface between the cathode and the oxidizing agent. The cathode preferably comprises a material that allows oxygen ions to migrate through the cathode to access the electrolyte. The cathode and the cathode current collector may also be operated at high temperatures, as previously described.

30 The cathode may be a solid state cathode, or the cathode may include liquid components, as previously described. Examples of solid state cathodes include a metal oxide cathode, a mixed metal oxide cathode, a perovskite-type oxide cathode, a metal cathode, or combinations thereof, all described above.

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In one embodiment, the current collector is operable when the cathodic material is at a temperature of less than about 1500 °C, preferably at a temperature of less than about 1300 °C, more preferably less than about 1200 °C. In another embodiment, the current collector is operable at temperatures of at least 200 °C or at least 300 °C, and preferably at temperatures of at least about 500 °C or about 800 °C. By “operable,” it is meant that the current collector is able to transfer electricity to or from the device. Other example operating temperature ranges where the current collector may be designed to be operable at include, but are not limited to, a temperature between about 200 °C to about 1500 °C, between about 300 °C to about 1500 °C, between about 500 °C to about 1300 °C, between about 500 °C to about 1200 °C, between about 500 °C to about 1000 °C, between about 600 °C to about 1000 °C, between about 700 °C to about 1000 °C, between about 800 °C to about 1000 °C, between about 500 °C to about 900 °C, between about 500 °C to about 800 °C, and between about 600 °C to about 800 °C. Other embodiments may include other temperature ranges. For example, the temperature range may be between about 1000 °C to about 1500 °C, between about 1500 °C to about 2000 °C, between about 2000 °C to about 2500 °C, between about 700°C to about 1300°C, between about 1200°C to about 1800°C, between about 1700°C to about 2300°, between about 1400°C to about 1700°C, or between about 300°C to about 2500°C.

In certain embodiments, the cathode and at least a portion of the cathode current collector may have similar or “matched” thermal expansion coefficients, for example, to reduce strain between the two components, or to reduce the likelihood of forming cracks in either component. In some embodiments, the cathode and the cathode current collector may be in deformable contact, for example, if the cathode and the cathode current collector are both designed to be solid during operation. Preferably, the cathode and the cathode current collector remain in deformable contact to maintain electronic communication over the entire temperature range of the device, such as between room temperature and the operating temperature. The cathode and the cathode current collector may be able to function for extended periods of use, which may be continuous or intermittent (e.g., the electrochemical device may be repeatedly activated and deactivated), for example, at least about 1 day, about 1 week, about 20 days, about 40 days, or even years or more. Ideally, the cathode current collector should be able to collect current under these operating conditions for an indefinite period of time.

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In one embodiment, contact can be maintained by matching the respective thermal expansion coefficients of the cathode and cathode current collector. The use of matched thermal expansion coefficients may minimize thermal stresses and prevent cracking of either component, especially during repeated use. For example, the thermal expansion coefficients between the cathode and the cathode current collector may differ by less than about 30% at a temperature of less than about 1500 °C or 1200 °C, preferably less than about 20% and more preferably less than about 10%. In one embodiment, the cathode current collector comprises substantially the same material as the cathode, and thus the respective thermal expansion coefficients would not theoretically differ. In another embodiment, the cathode current collector and the cathode may comprise different materials, but still have substantially similar thermal expansion coefficients, preferably over a wide temperature range, for example, between room temperature and the operating temperature. Other example temperature ranges include between about 250 °C and about 1200 °C, between about 500 °C and about 1200 °C, between about 800 °C and about 1200 °C, or between about 1000 °C and about 1600 °C.

Interconnects

As previously described, electrochemical devices of the invention may further comprise an interconnect that electronically connects the anode of a first cell with the cathode of a second cell. In certain embodiments, the interconnect may additionally connect several electrodes together electronically, for example, two or more anodes with a cathode, two or more cathodes with an anode, or several anodes to several cathodes. In some embodiments, an interconnect may be used to connect two or more anodes without necessarily electronically connecting the anodes to a cathode, or, conversely, to connect two or more cathodes without connecting them to an anode.

The interconnect may also convey thermal energy or gases towards or away from each electrochemical device, depending on the specific use. For example, the interconnect may have a flow of gas that allows oxygen or other gases to enter or leave the electrochemical device, and may preferentially direct the flow of gases towards or away from one of the electrodes, such as the anode. The interconnect may have any shape and sufficient electrical and thermal conductivity to achieve these functions.

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The interconnect may have any shape suitable for maintaining electronic communication between the anode and the cathode. Depending on the respective shapes of the anode and the cathode, the interconnect may be, for example, U-shaped (e.g., as is shown in Figs. 25 or 26), a linear rod, or, in embodiments where the anode and the cathode are positioned nearly adjacent to each other, the interconnect may be a short piece of material connecting the two devices (e.g., as is shown in Fig. 7). Other shapes, including irregular ones (e.g., as previously discussed above), are also contemplated. Electronic communication may be accomplished using any suitable means, including direct or indirect contact, i. e., through another material, or through deformable contact of the interconnect with either or both of the anode and the cathode. In other embodiments, the interconnect may be integrally connected to either or both of the anode and the cathode, or may conform with the shape of either the anode or the cathode, depending on the application. The shape of the interconnect may be chosen to maintain electronic contact during use of the electrical device, for example, over long periods of time, or as the device is heated and cooled in between uses. The shape may also be determined by other factors, such as the shape or arrangement of the cathode and anode within the device, or for ease of assembly.

In some embodiments, the interconnect may extend into or be integral to one or both of the cathode and the anode, for example, as shown in Fig. 27. This arrangement may be useful, for example, in situations where better electronic communication between the interconnect and the electrodes is desired, or to improve the transport of gases or other fluids into or out of the device. In certain embodiments, material from the anode or the cathode may be used within the interconnect, or as a component of the interconnect. In other embodiments, the interconnect may function and be used as a current collector within the device; thus, the interconnect may simultaneously collect a current from one cell and electronically communicate that current with an adjacent cell.

The interconnect may be made from any material or materials able to maintain electronic communication between the anode and the cathode, preferably at the operating temperatures of the device, as previously discussed. For example, the interconnect may be fashioned out of metals, alloys, ceramics, cermets, composites, or the like. Some examples of suitable materials may include, but are not limited to, copper, nickel, silver, stainless steel, tin, NIKROTHAL® (registered trademark of Bulten-Kanthal Aktiebolag Corp., Hallstahammar, Sweden), LSM, and the like, as well as alloys or cermets of these

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materials. Other example materials may include molybdenum, iridium, palladium, antimony, rhenium, bismuth, platinum, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, indium, thallium, cadmium, gadolinium, chromium, iron, tungsten, cobalt, zinc, or vanadium. Other ceramics that may be used include lanthanum
5 ceramics, strontium ceramics, and other ceramic materials described above, for example, lanthanum-calcium-chromium oxides. In some embodiments, a portion of the interconnect may be a liquid at the operating temperatures of the device, as long as electronic communication is maintained.

The interconnect may be constructed such that different portions of the device are
10 formed from different materials. For example, the interconnect may be fashioned out of an inner material and an outer sheathing material, or one region of the interconnect may be fashioned out of a first material (for example, for compatibility with the anode) while another region may be fashioned out of a different material (for example, for compatibility with the cathode or cathode environment, or to facilitate fluid transport
15 within the interconnect).

In certain embodiments, at least part of the interconnect may be fashioned out of materials not fully able to withstand the operating environment (for example, the material may melt or corrode during operation). In some embodiments, the interconnect may include a protective material able to protect the interior of the interconnect from the
20 external operating environment, e. g, to prevent corrosion of the interior. In other embodiments, the interconnect may include a containing material, for example, to contain components of the interconnect that liquefy during operation in embodiments where the interconnect is designed to include liquid components.

In some embodiments, the protective or containing material remains unreacted
25 during use; in other embodiments, the material may alloy or react with the inner material during operation to maintain the coherence or electronic conductivity of the interconnect. The material may be any of the materials described above that may be used in the construction of sheathing materials for current collectors (e.g., a metal oxide or a mixed metal oxide), or other materials that are able to contain the inner material and optionally
30 may be able to pass a current. As one example, the interconnect may consist of a silver center, contained by an LCC or a nickel chromium jacket. During use, the interconnect may be heated past the melting point of silver, but, due to the presence of the containing nickel chromium jacket, the interconnect remains coherent and is able to pass a current.

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In some embodiments, the interconnect may allow or be able to accept the entrance of certain substances into the interconnect. For example, external substances such as gases or other fluids, fuels, waste product, non-oxidizing agents, and the like may be able to enter the interconnect without preventing electronic communication
5 between the two electrodes. As one example, oxygen gas leaking into the interconnect may be transported to and consumed at the anode. As another example, fuel may be mixed in with the interconnect, for example, to facilitate fuel delivery to the electrical device, or to minimize the thickness of or prevent the formation of a passivation layer on cathode. The fuel may be the same or different from the fuel used to power the device.
10 Other agents, for example, a non-oxidizing agent such as a noble gas or a reducing gas, may also be able to enter the interconnect. The source of the non-oxidizing agent may be an external source, or from the anode or cathode.

In certain cases, the interconnect may also function, at least in part, to protect an electrode. As one specific example, oxygen may leak into the interconnect, for example,
15 through a joint or a crack. The oxygen may be consumed at the anode during operation of the device. However, at the cathode current collector, oxygen may not be desired and may, for example, react with the cathode current collector, reducing the ability of the cathode current collector to collect a current. The interconnect may be able to transport oxygen away from the cathode current collector and to the anode, for example, by
20 diffusion or convection.

To reduce the likelihood of forming cracks, the interconnect and an electrode such as the cathode may have, for example, similar or "matched" thermal expansion coefficients, or they may be in deformable contact. In one embodiment, the respective thermal expansion coefficients of the cathode and interconnect differ by less than about
25 30% at a temperature of less than about 1500 °C or 1200 °C, preferably less than about 20% and more preferably less than about 10%. In one embodiment, the interconnect comprises substantially the same material as the cathode, and thus the respective thermal expansion coefficients would theoretically not differ. In another embodiment, the interconnect and the cathode may comprise different materials, but still have
30 substantially similar thermal expansion coefficients, preferably over a wide temperature range, for example, between room temperature and the operating temperature. Other example temperature ranges include between about 250 °C and about 1200 °C, between about 500 °C and about 1200 °C, between about 800 °C and about 1200 °C, or between

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about 1000 °C and about 1600 °C. Preferably, the interconnect is able to function under these conditions for extended periods of time, for example, at least about 1 day, about 1 week, about 20 days, about 40 days, or even years or more. Ideally, the interconnect should be able to function under these operating conditions for an indefinite period of time.

In Figs. 5 and 6, interconnects 107 and 127 are shown as being positioned adjacent to cathodes 106 and 126, respectively, and the adjacent anodes. Fig. 7 shows a close-up of a stack of Fig. 5. In this figure, stack 100 features interconnect 107 positioned adjacent cathode 106. Interconnect 107 is also positioned adjacent an anode. Fig. 8 shows another example arrangement for connecting two tubular devices of the invention together to form a stack via an interconnect. Other arrangements of devices and interconnects can be readily determined by those of ordinary skill in the art.

Fig. 25 illustrates another configuration involving an interconnect. In Fig. 25, electrical device 600 has two electrical cells 605, 610. Each cell includes an anode current collector 625, 630, and a cathode having a cathode current collector 615, 620. Anodic material 645 surrounds anode current collector 625, and similarly, anodic material 650 surrounds anode current collector 630. Between the anodic material and the cathode is an electrolyte 635, 640. Interconnect 660 facilitates electronic communication between the cathode current collector 620 of cell 610 and anode current collector 625 of cell 605.

Also illustrated in Fig. 25 is vent 670. Vent 670 allows fluids to enter or leave cell 605. These fluids may include, for example, oxygen, fuel, or the like. In the particular embodiment shown in Fig. 25, a portion of vent 670 is in fluid communication with cathode current collector 620 of cell 610. For example, a fuel, a non-oxidizing agent such as an inert gas, or the like may be in fluid communication with cathode current collector 620.

In the embodiment of Fig. 25, external leakage of air or oxygen into the interconnect is represented by arrow 680. External leakage into the interconnect may occur, for example, through connections between interconnect 660 and cell 610, as shown by arrow 680 in Fig. 25, or through diffusion through the walls of the interconnect in certain cases. As one example, if the entering gas is oxygen or another oxidizing agent which, upon exposure to cathode current collector 620, may impede the function of the cathode current collector, then the entering agent may be dissolved within

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interconnect 660. The dissolved agent may then diffuse, in some embodiments rapidly, through interconnect 660 to anodic material 645, where it may react or otherwise be disposed of. Thus, in this embodiment, the dissolved agent does not have sufficient time to react with cathode current collector 620.

5 Other example embodiments of the invention are shown in Figs. 26 and 27. In these figures, certain parts of the invention have been removed for clarity. Fig. 26 shows two electrochemical cells 605, 610, connected by interconnect 660. As previously discussed, each cell has a cathode current collector 615, 620, and an anode current collector 625, 630. Each cell also contains anodic material 645, 650, and an electrolyte
10 635, 640. As shown in this figure, interconnect 660 represents a separate part of the electrochemical device. This configuration may be useful, for example, in a device having interchangeable parts, or when modular construction techniques are desired. Interconnect 660 maintains electronic communication between anode current collector 625 of cell 605 and cathode current collector 620 of cell 610. However, in other
15 embodiments, the interconnect may be an integral part of one of the cells, for instance, as shown in Fig. 27. In this example, anodic material 645 simultaneously functions as anodic material and as part of the interconnect material. This configuration may be useful, for example, in maintaining better electronic communication between the anode and the cathode of adjacent cells, or when simpler construction is desired.

20

The function and advantage of these and other embodiments of the present invention will be more fully understood from the examples below. The following examples are intended to illustrate the benefits of the present invention, but do not exemplify the full scope of the invention.

25

EXAMPLES

Example 1

This example illustrates one method of making an embodiment of the invention.

30

In one embodiment, the main conductor of the current collector consisted of a pure molybdenum rod, 25 cm long and 0.317 cm in diameter. A cylindrical jacket, made of LCC ($\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}$ oxide) with a raw thickness of 400 μm was formed to act as a

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sheathing layer. This jacket was approximately 5 mm in outer diameter and was closed at one end. This jacket encapsulated one end of the molybdenum rod.

Approximately 1.6 g of tin were melted and inserted between the LCC jacket and the molybdenum rod, providing electrical contact between the jacket and the rod. A 15
5 cm long alumina tube, 5 mm in outer diameter and 4 mm in inner diameter, was then slid down from the other end of the molybdenum rod, and a small dab of high purity alumina cement was applied to the area at the other end of the LCC jacket. The alumina was pushed down until it contacted the open end of the LCC jacket, the glue and the finish joint providing a bond between the LCC jacket, the alumina tube, and the molybdenum
10 rod. After the glue had cured, the current collector was finished.

When tested in a manner similar to that described in Example 2, the resistance was found to be less than 0.015 Ω .

Thus, this example illustrates one method of making an embodiment of this invention.

15

Example 2

In this example, an embodiment of this invention was used to collect an electrical current.

A current collector was prepared using a method similar to that described in
20 Example 1. To use the current collector, 3 cm of the 4 cm long LCC jacket was inserted into a molten tin bath located in an electrochemical device. The alumina sheathing prevented tin splash from coming into contact with the molybdenum rod. Electrical connections were made to the exposed molybdenum rod outside the electrochemical device, using copper wire and conventional connectors. When used in conjunction with
25 an electrochemical device at 1000 °C, the resistance of the entire current collector assembly during current collection was found to be less than 0.010 Ω .

Thus, this example illustrates how an embodiment of the invention may be used to collect a current.

Example 3

This example illustrates another method of making an embodiment of the invention.

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In this example, the main conductor of the current collector consisted of a pure nickel rod, 25 cm long and 0.317 cm in diameter. A cylindrical jacket, made of LCC ($\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}$ oxide) with a raw thickness of 400 μm was formed to act as a sheathing layer for the nickel. This jacket was approximately 5 mm in outer diameter, 5 cm in length, and was closed at one end. This jacket encapsulated one end of the nickel rod.

A copper carbon glue mixture was made using 20 weight percent graphite and 80 weight percent copper with a ceramic glue thinner. This glue was inserted between the LCC jacket and the nickel rod, providing electrical contact between the jacket and the rod. A 15 cm long alumina tube, 5 mm in outer diameter and 4 mm in inner diameter, was then slid down from the other end of the nickel rod, and a small dab of high purity alumina cement was applied to the area at the back end of the LCC jacket. The alumina was pushed down until it contacted the open end of the LCC jacket, the glue providing a bond between the LCC jacket, the alumina tube, and the nickel rod. After the glue and the cement had cured, the current collector was finished.

When tested in a manner similar to that described in Example 2, the initial resistance was found to be less than 0.150 Ω .

Thus, this example illustrates another method of making an embodiment of this invention.

20 Example 4

This example illustrates one method of making an embodiment of the invention.

In one embodiment, the main conductor of the current collector was formed of multiple oxygen-free copper strands (0.020 cm – 0.016 cm diameter, or 32 – 34 American Wire Gauge) approximating a wire of about 0.26 cm in diameter (i.e., a single 10 Gauge wire) centered around a single piece of 0.159 cm diameter (1/16 inch) copper tubing. A 7 cm cylindrical jacket, made of LCC (specifically, $\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}$ oxide in this example) with a thickness of about 400 μm was formed to act as a sheathing layer. This jacket was approximately 5 mm in outer diameter and was closed at one end. The jacket encapsulated one end of the copper wire and tubing. A 5 – 10 μm nickel layer was deposited via electroplating on the inside of the jacket.

The assembly of the current collector was as follows. The stranded copper wire was first inserted into the nickel plated jacket. Then, a 30 cm (1 foot) section of copper tubing was inserted into the center of the jacket and strand assembly, until the tubing was

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within about 2 mm of the bottom of the jacket. The copper tubing was sharpened with a 45° cut to facilitate insertion. A roughly 24 cm long alumina tube (inner diameter of 6 mm, outer diameter of 7 mm) was then slid over the exposed copper strand until the tube overlapped the LCC jacket by 0.5 – 1 cm. The overlap was filled with a high purity alumina cement. The total protected length from the LCC jacket to the end of the alumina was approximately 30 cm.

Thus, this example illustrates another method of making an embodiment of this invention.

While several embodiments of the invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and structures for performing the functions and/or obtaining the results or advantages described herein, and each of such variations or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art would readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that actual parameters, dimensions, materials, and configurations will depend upon specific applications for which the teachings of the present invention are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described. The present invention is directed to each individual feature, system, material and/or method described herein. In addition, any combination of two or more such features, systems, materials and/or methods, if such features, systems, materials and/or methods are not mutually inconsistent, is included within the scope of the present invention.

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Claims

1. An electrical device, comprising:
a current collector comprising an electrically conducting material and
5 a sheathing material surrounding at least a portion of the electrically
conducting material, the sheathing material comprising an element selected
from the group consisting of scandium, yttrium, titanium, tin, indium,
aluminum, zirconium, iron, cobalt, manganese, strontium, calcium,
magnesium, barium, beryllium, a lanthanide, chromium, and combinations
10 thereof.
2. The electrical device of claim 1, wherein the current collector is an anode
current collector.
- 15 3. The electrical device of claim 1, wherein the current collector is a cathode
current collector.
4. The electrical device of claim 1, wherein the current collector comprises
anodic material.
- 20 5. The electrical device of claim 1, wherein the current collector comprises
cathodic material.
6. The electrical device of claim 1, wherein the electrically conducting material
25 comprises an element selected from the group consisting of molybdenum,
iron, tungsten, tantalum, ruthenium, nickel, copper, chromium, manganese,
gold, silver, platinum, steel, stainless steel, graphite, cobalt, and combinations
thereof.
- 30 7. The electrical device of claim 1, wherein the electrically conducting material
comprises a metal.

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8. The electrical device of claim 7, wherein the metal is selected from the group consisting of molybdenum, iron, tungsten, tantalum, ruthenium, nickel, copper, chromium, cobalt, aluminum, manganese, phosphorous, carbon, steel, stainless steel, a superalloy, platinum, gold, silver, palladium, rhodium, osmium, and alloys thereof.
- 5
9. The electrical device of claim 1, wherein the current collector further comprises an inner material disposed between at least a portion of the electrically conducting material and at least a portion of the sheathing material.
- 10
10. The electrical device of claim 9, wherein the inner material comprises a plurality of bristles.
11. The electrical device of claim 9, wherein the inner material comprises a fiber.
- 15
12. The electrical device of claim 9, wherein the inner material comprises a metal.
13. The electrical device of claim 12, wherein the metal is liquid at temperatures at which the electrical device is designed to operate.
- 20
14. The electrical device of claim 12, wherein the metal has a melting point of greater than about 200 °C.
- 25
15. The electrical device of claim 14, wherein the metal has a melting point of greater than about 300 °C.
16. The electrical device of claim 15, wherein the metal has a melting point of greater than about 500 °C.
- 30
17. The electrical device of claim 16, wherein the metal has a melting point of greater than about 750 °C.

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18. The electrical device of claim 17, wherein the metal has a melting point of greater than about 1000 °C.
- 5 19. The electrical device of claim 12, wherein the metal comprises at least one element selected from the group consisting of tantalum and niobium.
20. The electrical device of claim 12, wherein the metal comprises a noble metal.
- 10 21. The electrical device of claim 20, wherein the noble metal comprises a metal selected from the group consisting of platinum, gold, silver, rhenium, rhodium, palladium, iridium, osmium, and combinations thereof.
22. The electrical device of claim 12, wherein the metal comprises tin.
- 15 23. The electrical device of claim 12, wherein the metal comprises an element selected from the group consisting of copper, molybdenum, iridium, palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, indium, thallium, cadmium, gadolinium, chromium, nickel, iron, tungsten, cobalt, zinc, vanadium and alloys thereof.
- 20 24. The electrical device of claim 1, wherein the sheathing material comprises a boride.
- 25 25. The electrical device of claim 24, wherein the boride comprises an element selected from the group consisting of titanium, zirconium, hafnium, tantalum, niobium, and combinations thereof.
- 30 26. The electrical device of claim 1, wherein the sheathing material comprises a carbide.

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27. The electrical device of claim 26, wherein the carbide comprises an element selected from the group consisting of titanium, tantalum, zirconium, niobium, silicon, tungsten, and combinations thereof.
- 5 28. The electrical device of claim 1, wherein the sheathing material comprises a nitride.
29. The electrical device of claim 28, wherein the nitride comprises an element selected from the group consisting of zirconium, chromium, aluminum,
10 titanium, aluminum, carbon, and combinations thereof.
30. The electrical device of claim 1, wherein the sheathing material comprises a metal oxide.
- 15 31. The electrical device of claim 30, wherein the metal oxide comprises a compound selected from the group consisting of a lanthanum-strontium-manganese oxide, a lanthanum-strontium-iron oxide, a lanthanum-strontium-chromium oxide, a lanthanum-calcium-chromium oxide, a lanthanum-strontium-titanium oxide, a strontium-titanium-niobium oxide, a cerium-niobium oxide, a cerium-samarium oxide, a cerium-yttrium oxide, a cerium-gadolinium oxide, a yttria-stabilized zirconium oxide, a scandia-stabilized zirconia, an indium oxide, a tin oxide, and combinations thereof.
- 20 32. The electrical device of claim 30, wherein the metal oxide comprises an element selected from the group consisting of lanthanum, strontium, manganese, iron, cobalt, aluminum, chromium, calcium, titanium, niobium, cerium, samarium, yttrium, gadolinium, indium, zirconium, scandium, tin and combinations thereof.
- 25 33. The electrical device of claim 1, wherein the sheathing material comprises a ceramic.
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34. The electrical device of claim 1, wherein the sheathing material comprises a cermet.
35. The electrical device of claim 34, wherein the cermet comprises a first
5 material selected from the group consisting of copper, silver, platinum, gold, nickel, iron, cobalt, tin, indium and combinations thereof, and a second material selected from the group consisting of a zirconium oxide, an aluminum oxide, an iron oxide, a nickel oxide, a lanthanum oxide, a calcium oxide, a chromium oxide, a silicate, a glass, and combinations thereof.
- 10 36. The electrical device of claim 1, wherein the sheathing material is able to inhibit oxidation of the electrically conducting material.
37. The electrical device of claim 1, wherein the sheathing material comprises a
15 coating.
38. The electrical device of claim 37, wherein the coating comprises a metal selected from the group consisting of nickel, copper, gold, platinum, silver, rhodium, rhenium, osmium, palladium, and combinations thereof.
- 20 39. The electrical device of claim 1, wherein the current collector further comprises a second sheathing material disposed around at least a portion of the sheathing material.
- 25 40. The electrical device of claim 39, wherein the current collector further comprises a third sheathing material disposed around at least a portion of the first sheathing material.
- 30 41. The electrical device of claim 1, wherein the sheathing material has an erosion rate of less than about 1.8 centimeters per year during operation of the electrical device.

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42. The electrical device of claim 41, wherein the sheathing material has an erosion rate of less than about 1 centimeter per year during operation of the electrical device.
- 5 43. The electrical device of claim 41, wherein the sheathing material has an erosion rate of less than about 1 millimeter per year during operation of the electrical device.
- 10 44. The electrical device of claim 1, wherein a temperature at which the electrical device is designed to operate is greater than about 300 °C.
45. The electrical device of claim 44, wherein the temperature at which the electrical device is designed to operate is greater than about 500 °C.
- 15 46. The electrical device of claim 45, wherein the temperature at which the electrical device is designed to operate is greater than about 750 °C.
47. The electrical device of claim 46, wherein the temperature at which the electrical device is designed to operate is greater than about 1000 °C.
- 20 48. The electrical device of claim 1, wherein the sheathing material has an electrical conductivity of at least about 0.001 S/cm.
49. The electrical device of claim 48, wherein the sheathing material has an electrical conductivity of at least about 0.01 S/cm.
- 25 50. The electrical device of claim 49, wherein the sheathing material has an electrical conductivity of at least about 0.1 S/cm.
- 30 51. The electrical device of claim 50, wherein the sheathing material has an electrical conductivity of at least about 1 S/cm.

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52. The electrical device of claim 51, wherein the sheathing material has an electrical conductivity of at least about 10 S/cm.
53. The electrical device of claim 52, wherein the sheathing material has an
5 electrical conductivity of at least about 100 S/cm.
54. The electrical device of claim 1, further comprising a structure disposed around at least a portion of the electrically conducting material.
- 10 55. The electrical device of claim 54, wherein the structure comprises a material selected from the group consisting of an aluminum oxide, a silicate, a zirconium oxide, and combinations thereof.
56. The electrical device of claim 54, wherein the structure is constructed and
15 arranged to prevent a liquid substance external to the current collector from contacting the electrically conducting material.
57. The electrical device of claim 1, wherein the current collector further comprises a structure able to vent a gas from the current collector.
20
58. The electrical device of claim 57, wherein the structure is in fluid communication with the electrically conducting material.
59. The electrical device of claim 1, wherein the electrically conducting material
25 is liquid at a temperature at which the electrical device is designed to operate.
60. The electrical device of claim 59, wherein the electrically conducting material comprises a first metal selected from the group consisting of copper, molybdenum, iridium, palladium, antimony, rhenium, bismuth, platinum,
30 silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, chromium, nickel, iron, tungsten, cobalt, zinc, vanadium, gallium, aluminum, and alloys thereof.

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61. The electrical device of claim 60, wherein the current collector further comprises a second metal alloyed with the first metal.
- 5 62. The electrical device of claim 61, wherein the alloy of the first metal and the second metal is liquid at temperatures at which the device is designed to operate.
- 10 63. The electrical device of claim 60, wherein the current collector comprises a second metal which, at a temperature at which the device is designed to operate, does not substantially dissolve the first metal.
- 15 64. The electrical device of claim 63, wherein the second metal comprises an element selected from the group consisting of molybdenum, tungsten, carbon, titanium, and combinations thereof.
65. The electrical device of claim 1, wherein the current collector is able to oxidize a fuel.
- 20 66. The electrical device of claim 65, wherein the fuel comprises carbonaceous material.
67. The electrical device of claim 65, wherein the fuel comprises H₂.
- 25 68. The electrical device of claim 1, further comprising an anode in electronic communication with the current collector.
69. The electrical device of claim 1, further comprising a cathode in electronic communication with the current collector.
- 30 70. The electrical device of claim 1, further comprising an electrode having an overall thermal expansion coefficient, wherein the sheathing material has an overall thermal expansion coefficient substantially equal to the overall thermal expansion coefficient of the electrode.

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71. The electrical device of claim 1, further comprising an electrode in electronic communication with the current collector, the electrode having a composition different from the current collector and an overall thermal expansion coefficient, wherein the overall thermal expansion coefficient of the electrode and an overall thermal expansion coefficient of the current collector are within about 30% at a temperature between about 800 °C and about 1200 °C.
72. The electrical device of claim 71, wherein the overall thermal expansion coefficient of the electrode and the overall thermal expansion coefficient of the current collector are within about 20%.
73. The electrical device of claim 72, wherein the overall thermal expansion coefficient of the electrode and the overall thermal expansion coefficient of the current collector are within about 10%.
74. The electrical device of claim 71, wherein the electrode is a cathode.
75. The electrical device of claim 71, wherein the electrode is an anode.
76. The electrical device of claim 71, wherein the overall thermal expansion coefficient of the current collector and the overall thermal expansion coefficient of the electrode are substantially equal at a temperature between about 500 °C and about 1200 °C.
77. The electrical device of claim 76, wherein the overall thermal expansion coefficient of the current collector and the overall thermal expansion coefficient of the electrode are substantially equal at a temperature between about 250 °C and about 1200 °C.
78. The electrical device of claim 1, wherein the current collector is constructed and arranged to resist oxidation when exposed to an oxidative environment having a temperature of greater than about 800 °C.

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79. The electrical device of claim 1, wherein the electrically conducting material is constructed and arranged to resist oxidation when exposed to an oxidative environment having a temperature of greater than about 800 °C.
- 5 80. The electrical device of claim 1, wherein the sheathing material has a specific power loss of less than about 100 W/cm².
- 10 81. The electrical device of claim 80, wherein the sheathing material has a specific power loss of less than about 100 W/cm² at a temperature of at least about 300 °C.
82. The electrical device of claim 80, wherein the current collector has a specific power loss of less than about 1 W/cm².
- 15 83. The electrical device of claim 82, wherein the current collector has a specific power loss of less than about 0.01 W/cm².
- 20 84. The electrical device of claim 83, wherein the current collector has a specific power loss of less than about 0.0001 W/cm².
85. The electrical device of claim 1, wherein the current collector is a wire-form current collector.
- 25 86. The electrical device of claim 85, wherein the wire-form current collector is in deformable contact with an electrode.
87. The electrical device of claim 86, wherein the electrode is a cathode.
- 30 88. The electrical device of claim 86, wherein the electrode is an anode.
89. The electrical device of claim 85, wherein the current collector comprises a plurality of bristles.

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90. The electrical device of claim 85, wherein the current collector comprises a felt.
- 5 91. The electrical device of claim 85, wherein the current collector comprises a braid of wires.
92. The electrical device of claim 85, wherein the current collector comprises stranded wire.
- 10 93. The electrical device of claim 1, wherein the electrically conducting material is constructed and arranged to conduct electricity when the sheathing material is exposed to a reducing environment comprising a liquid metal.
- 15 94. The electrical device of claim 93, wherein the reducing environment is produced by a fuel cell comprising a solid electrolyte.
95. The electrical device of claim 93, wherein the liquid metal comprises tin.
- 20 96. The electrical device of claim 93, wherein the liquid metal comprises an element selected from the group consisting of copper, molybdenum, iridium, palladium, tin, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, indium, thallium, cadmium, chromium, nickel, iron, tungsten, cobalt, zinc, vanadium, gallium, aluminum, and alloys thereof.
- 25 97. The electrical device of claim 93, wherein the liquid metal is at a temperature of greater than about 300 °C.
- 30 98. The electrical device of claim 97, wherein the liquid metal is at a temperature of greater than about 500 °C.

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99. The electrical device of claim 98, wherein the liquid metal is at a temperature of greater than about 750 °C.
100. The electrical device of claim 99, wherein the liquid metal is at a temperature
5 of greater than about 1000 °C.
101. The electrical device of claim 1, further comprising
a source of a non-oxidizing agent in fluid communication with the current
collector.
102. The electrical device of claim 101, wherein the source of non-oxidizing agent
10 comprises a source of an inert gas.
103. The electrical device of claim 101, wherein the source of non-oxidizing agent
15 is in fluid communication with an anode.
104. The electrical device of claim 101, wherein the source of non-oxidizing agent
comprises an exhaust gas from an electrochemical reaction.
- 20 105. The electrical device of claim 101, wherein source of non-oxidizing agent
comprises a source of a reducing agent.
106. The electrical device of claim 105, wherein the reducing agent comprises a
compound selected from the group consisting of H₂, CO and a hydrocarbon.
- 25 107. The electrical device of claim 105, wherein the source of reducing agent
comprises a source of fuel.
108. The electrical device of claim 107, wherein the source of fuel is able to
30 supply fuel to an anode of the electrical device.
109. The electrical device of claim 107, wherein the source of fuel comprises a
source of a carbonaceous material.

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110. The electrical device of claim 1, further comprising:
a first electrochemical cell comprising a cathode; and
a second electrochemical cell comprising an anode;
5 wherein the current collector electronically interconnects the anode
and the cathode.
111. The electrical device of claim 110, wherein the current collector comprises a
metal that is liquid at temperatures at which the electrical device is designed
10 to operate.
112. The electrical device of claim 111, wherein the metal is selected from the
group consisting of copper, molybdenum, iridium, palladium, antimony,
rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium,
15 osmium, gold, lead, germanium, tin, indium, thallium, cadmium, chromium,
nickel, iron, tungsten, cobalt, zinc, vanadium, aluminum, gallium, and alloys
thereof.
113. The electrical device of claim 111, wherein the metal comprises material from
20 the anode.
114. The electrical device of claim 111, wherein the temperature at which the
device is designed to operate is greater than about 300 °C.
- 25 115. The electrical device of claim 114, wherein the temperature at which the
device is designed to operate is greater than about 500 °C.
116. The electrical device of claim 115, wherein the temperature at which the
device is designed to operate is greater than about 750 °C.
30
117. The electrical device of claim 116, wherein the temperature at which the
device is designed to operate is greater than about 1000 °C.

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118. The electrical device of claim 110, wherein the current collector deformably contacts the cathode.
119. The electrical device of claim 110, wherein the current collector deformably
5 contacts the anode.
120. The electrical device of claim 1, wherein the current collector is able to resist corrosion when exposed to an oxidative environment having a temperature of greater than about 800 °C.
10
121. The electrical device of claim 120, wherein the temperature of the oxidative environment is greater than about 1000 °C.
122. The electrical device of claim 120, wherein the current collector is able to
15 resist corrosion for at least about 24 hours.
123. The electrical device of claim 122, wherein the current collector is able to resist corrosion for at least about 7 days.

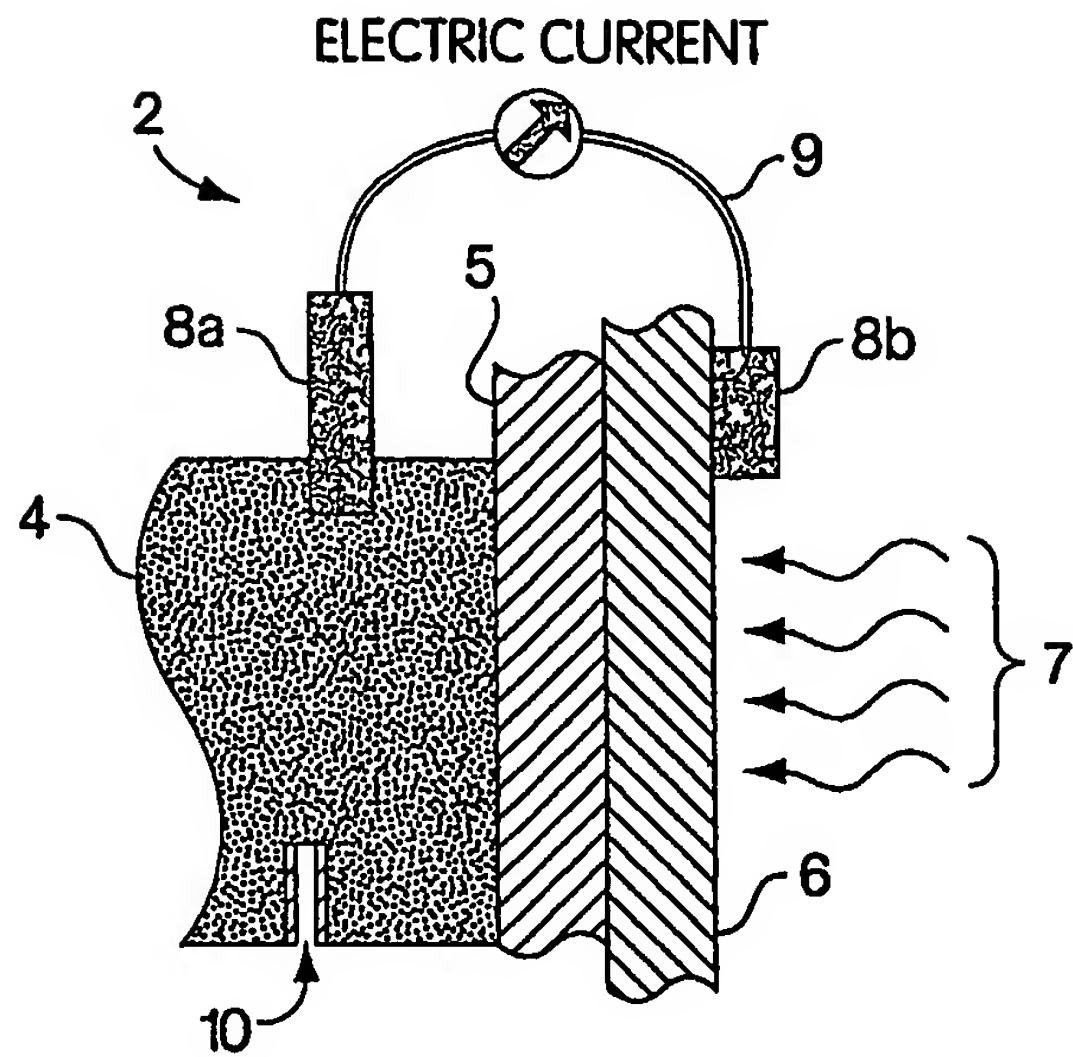


Fig. 1

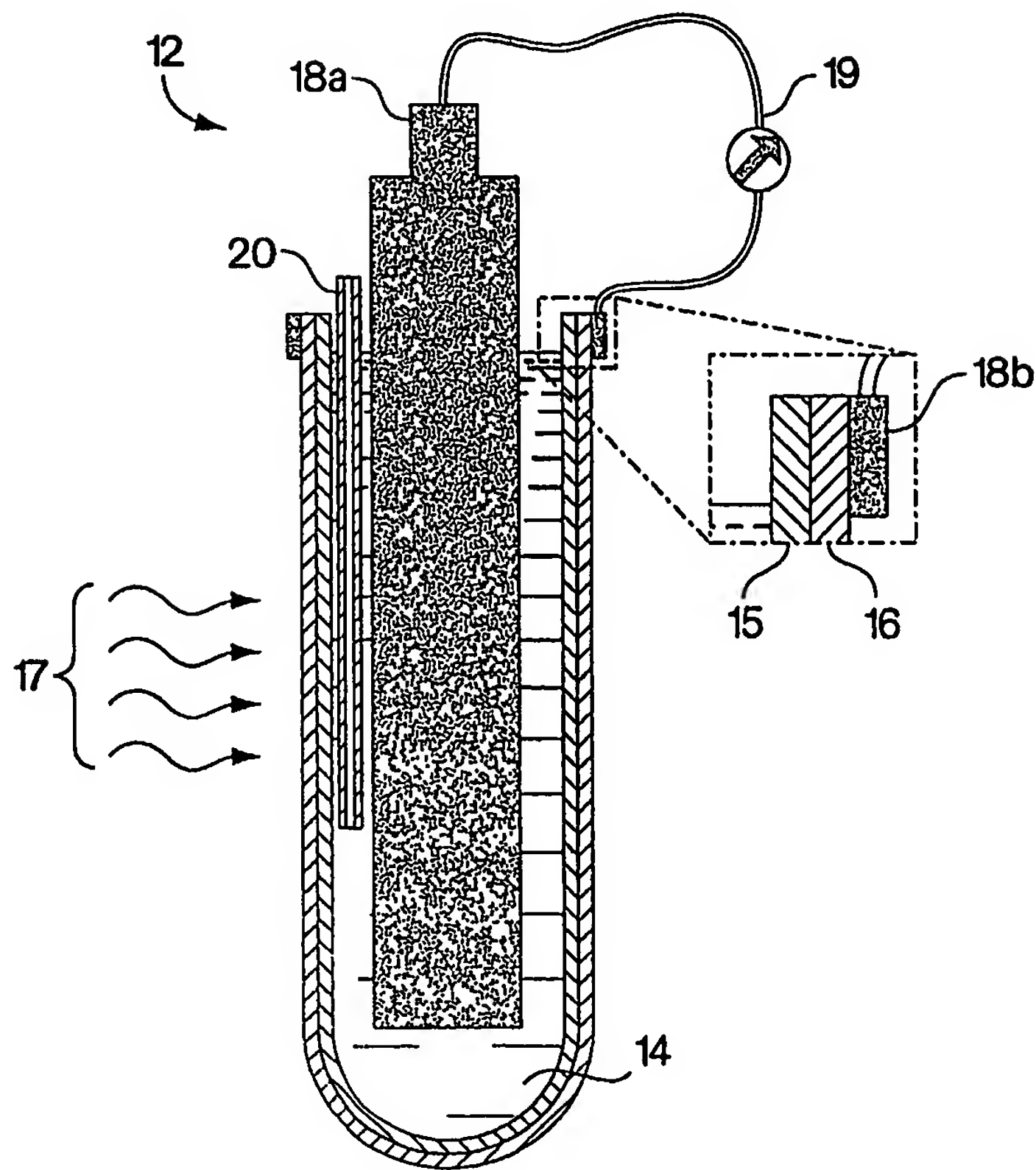


Fig. 2

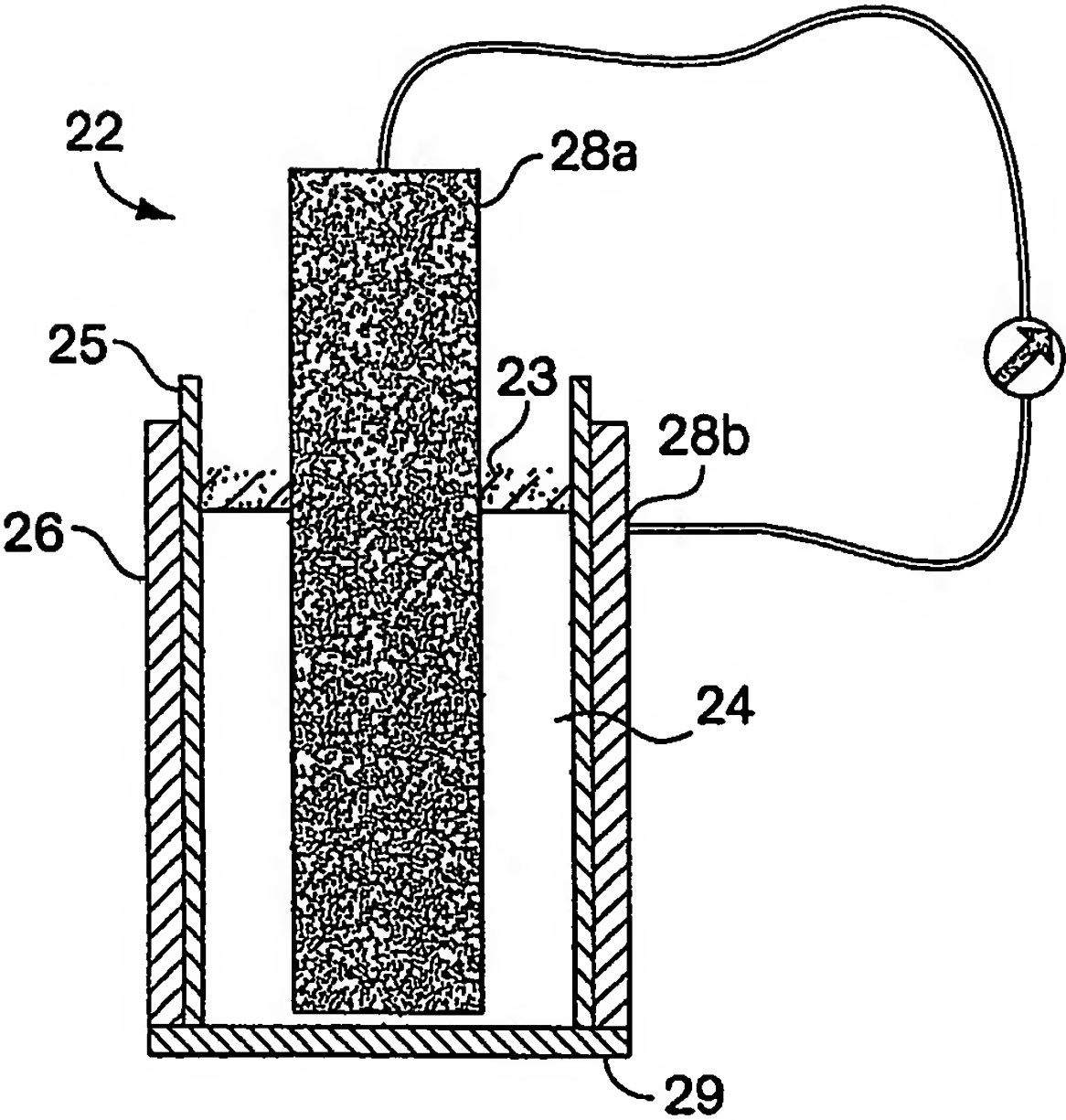


Fig. 3

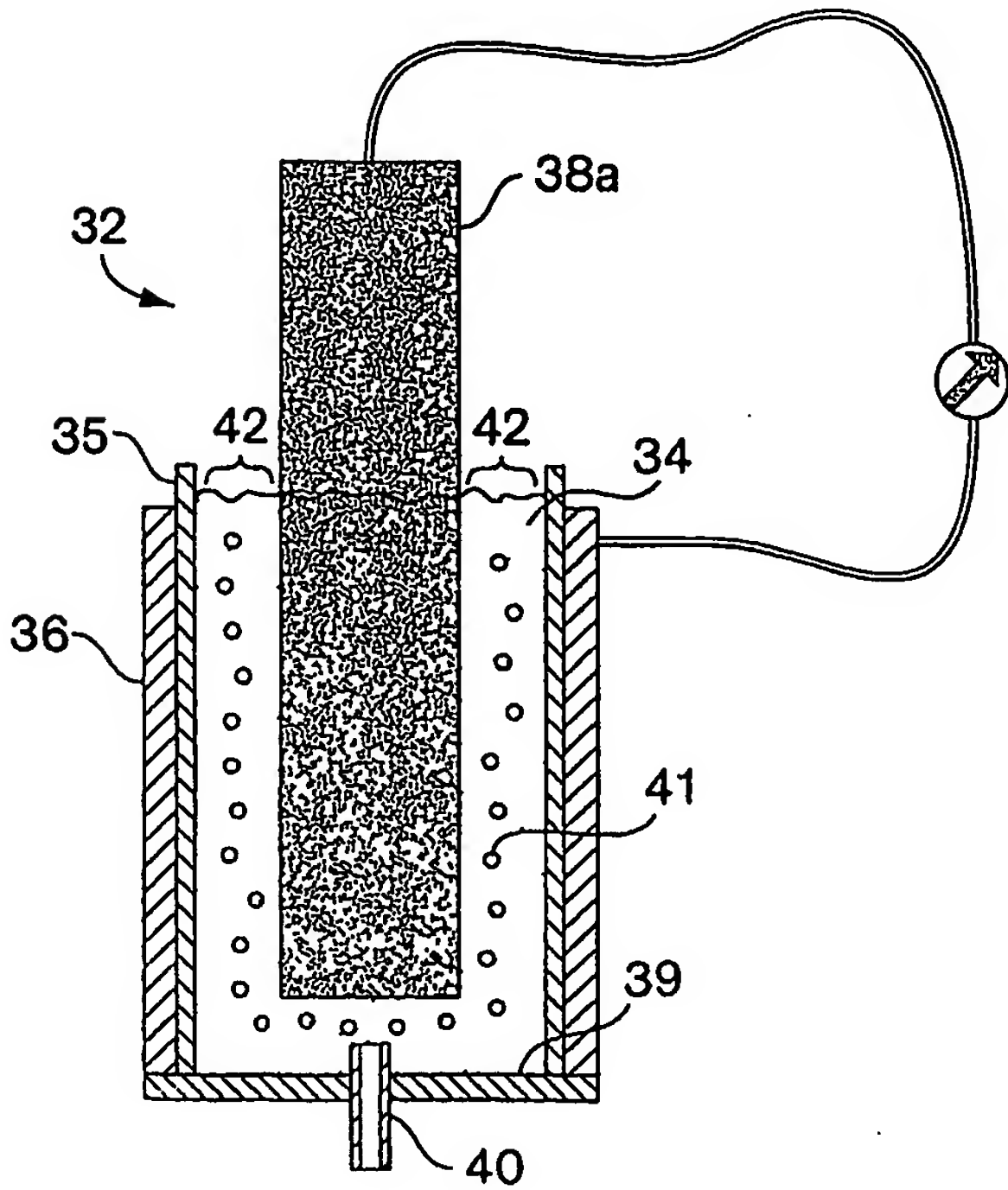


Fig. 4

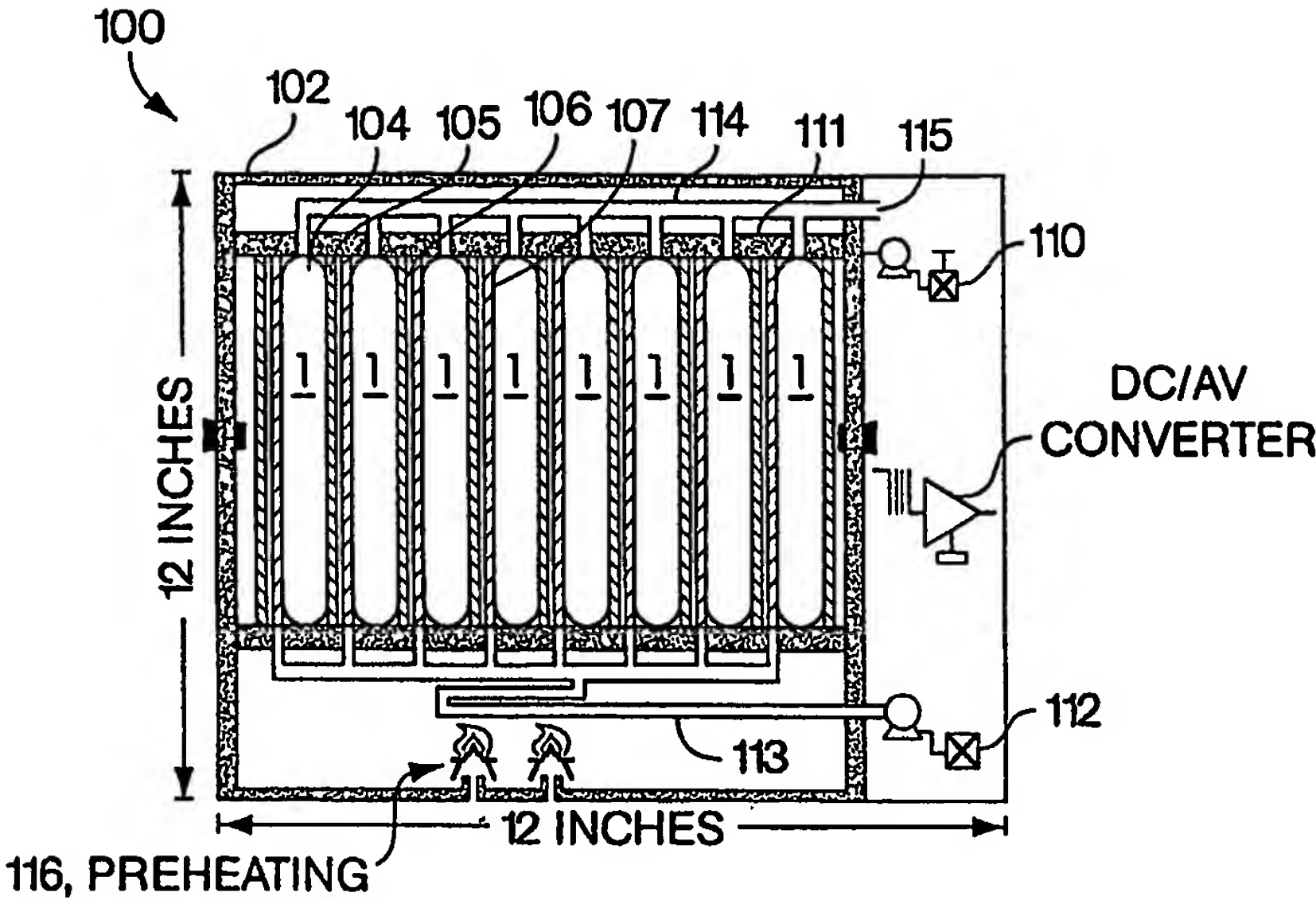


Fig. 5

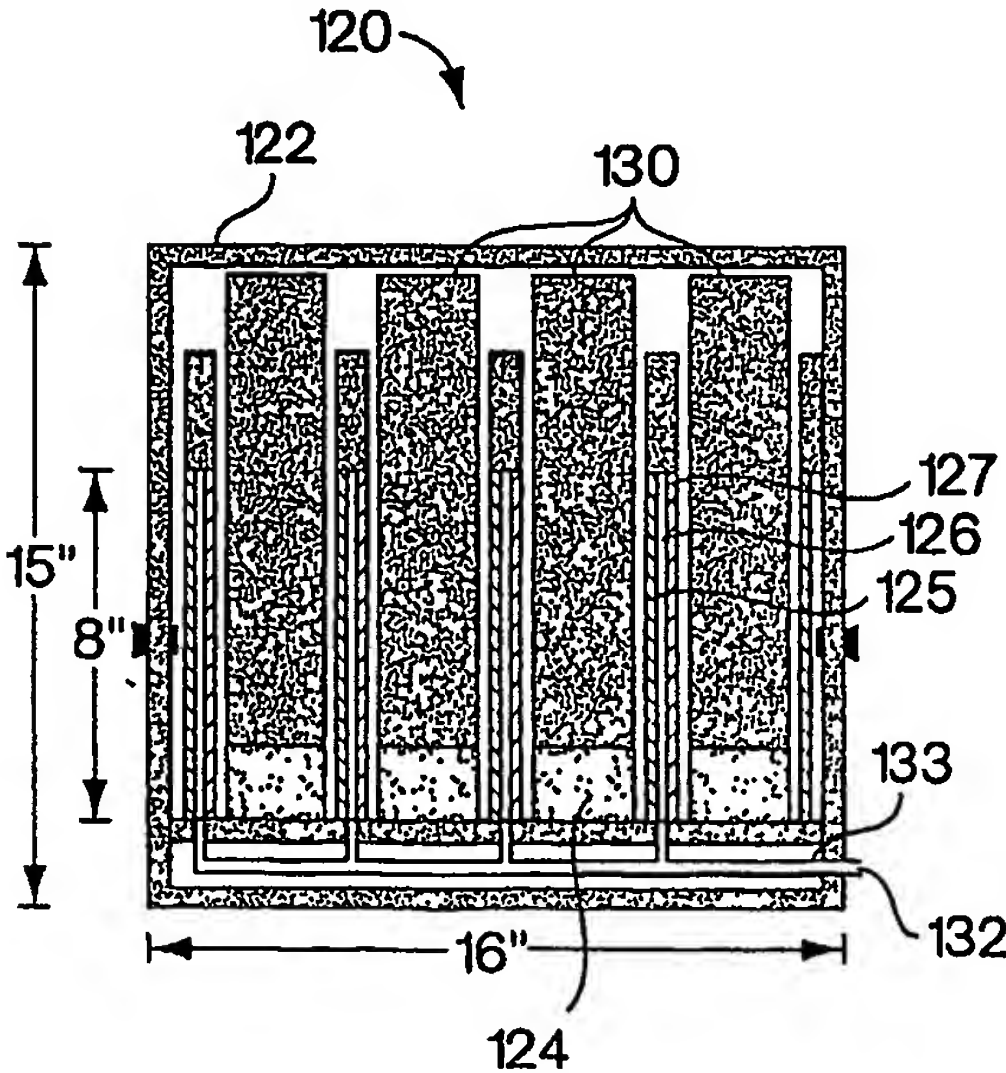


Fig. 6

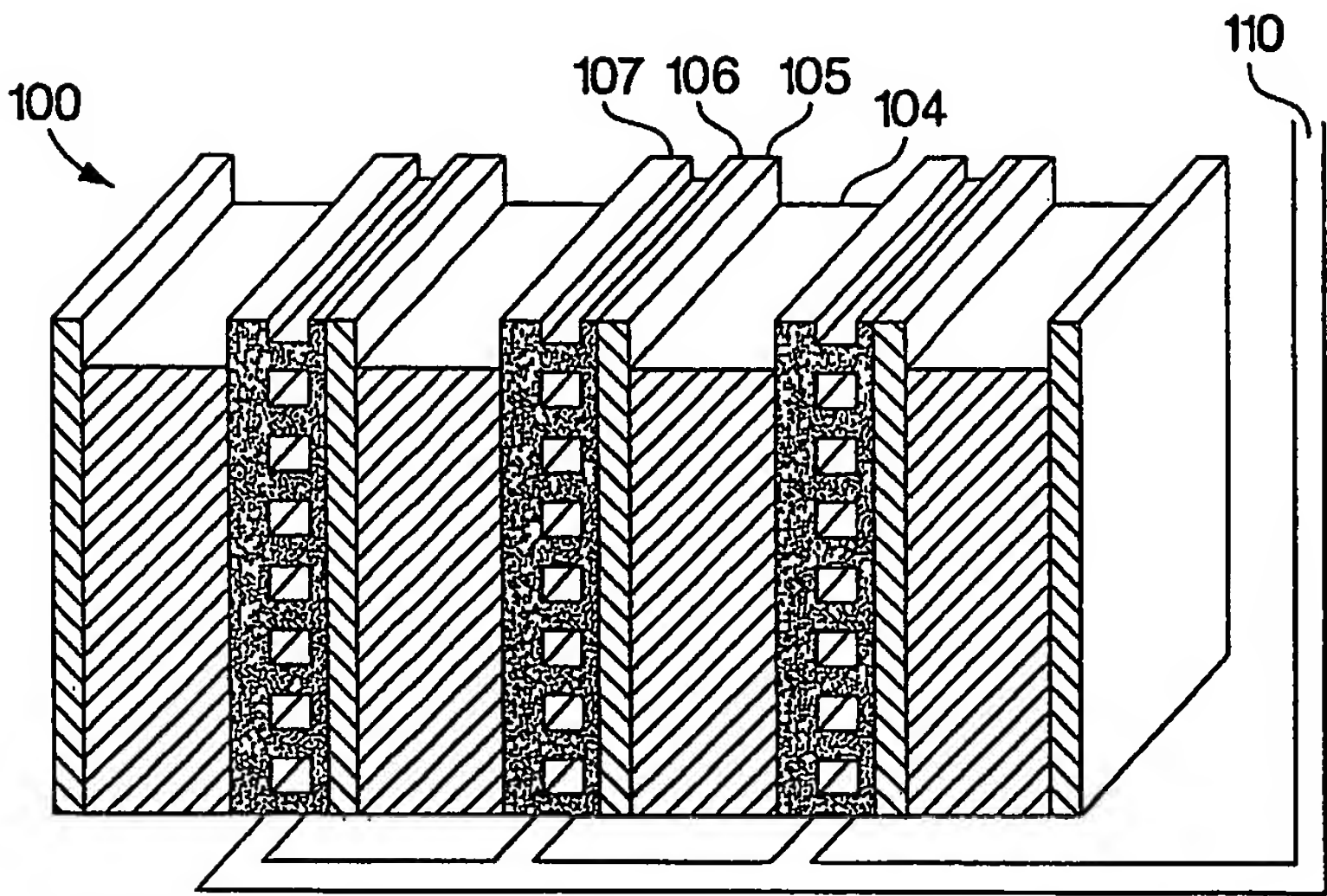


Fig. 7

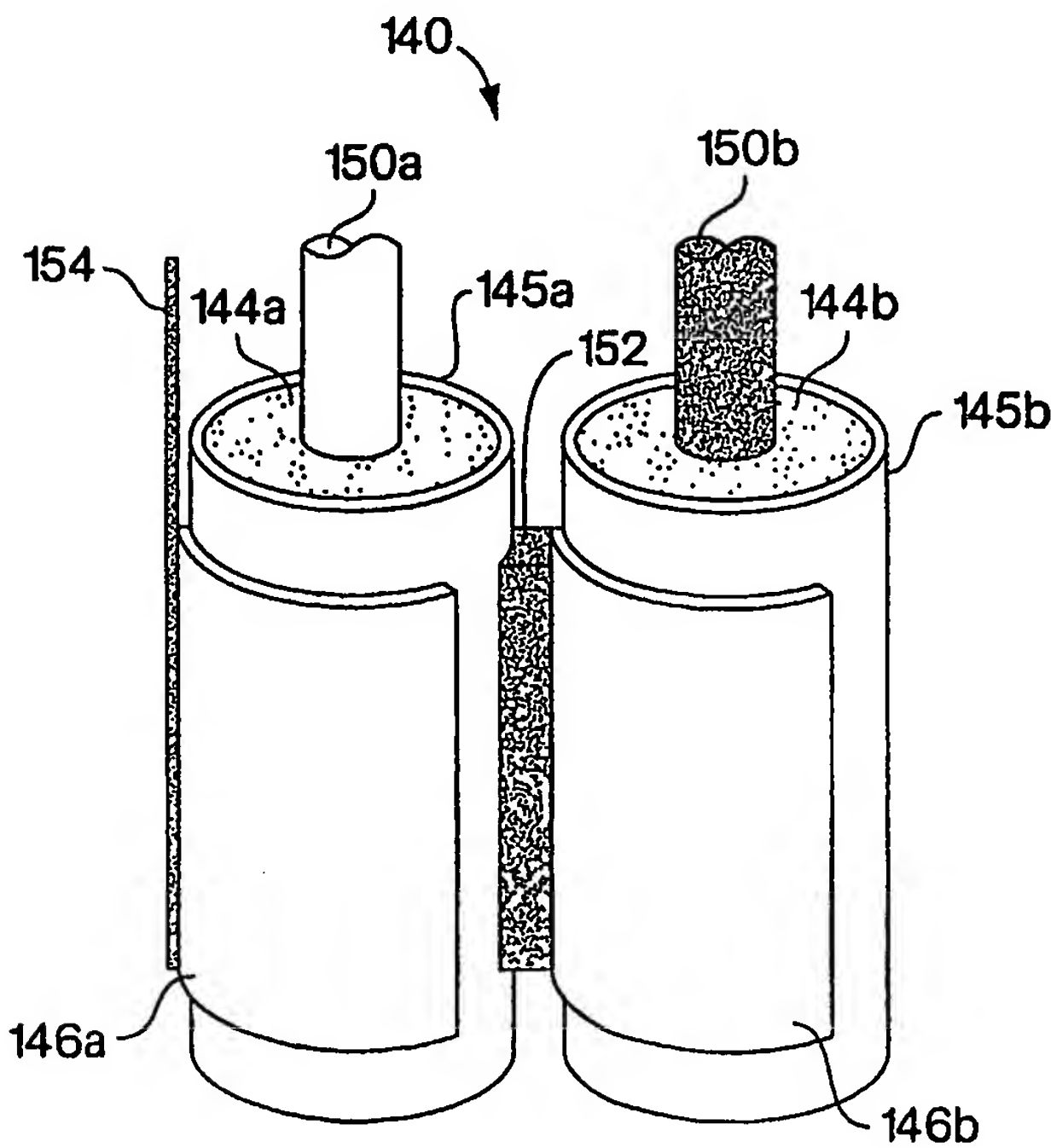


Fig. 8

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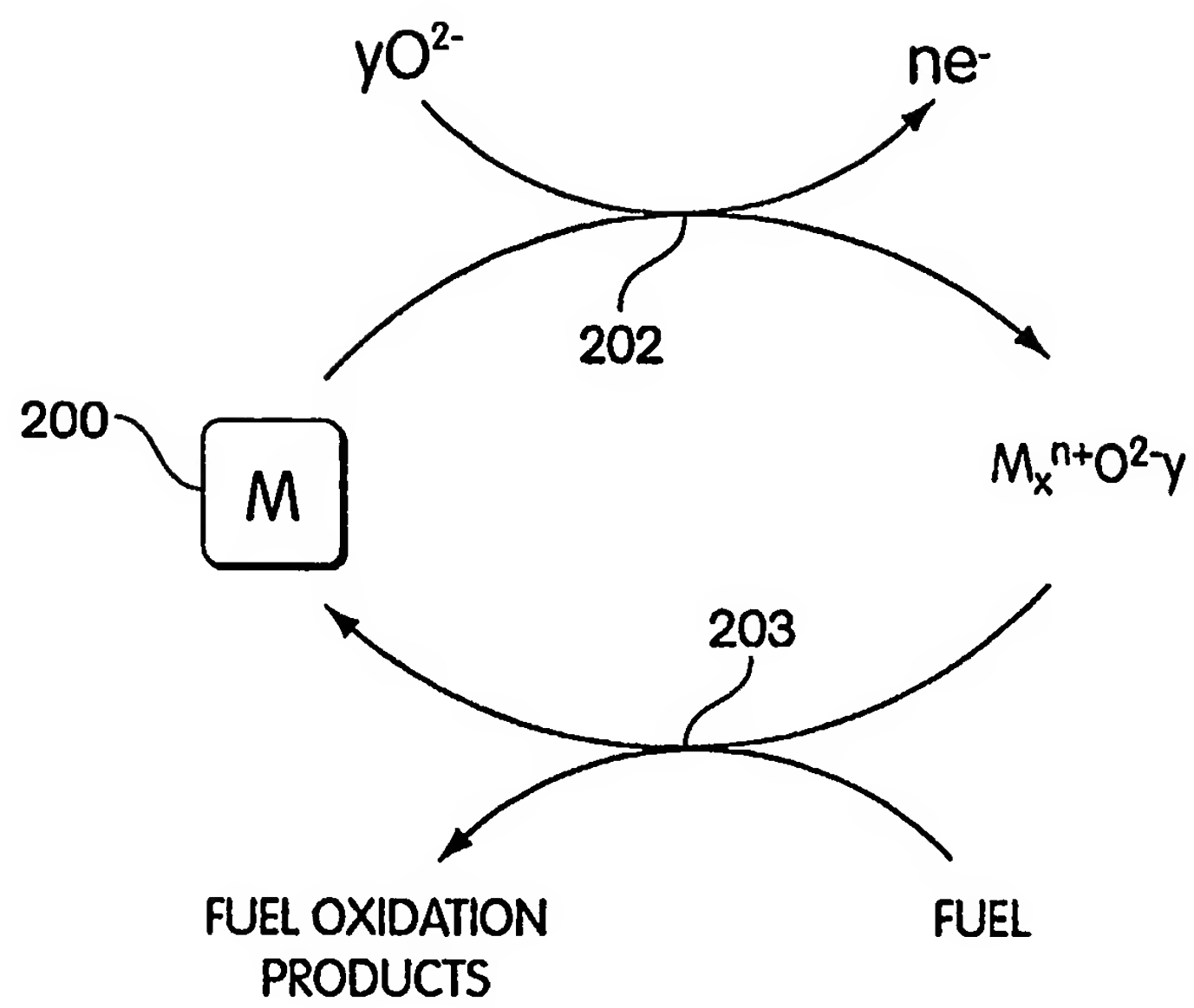


Fig. 9

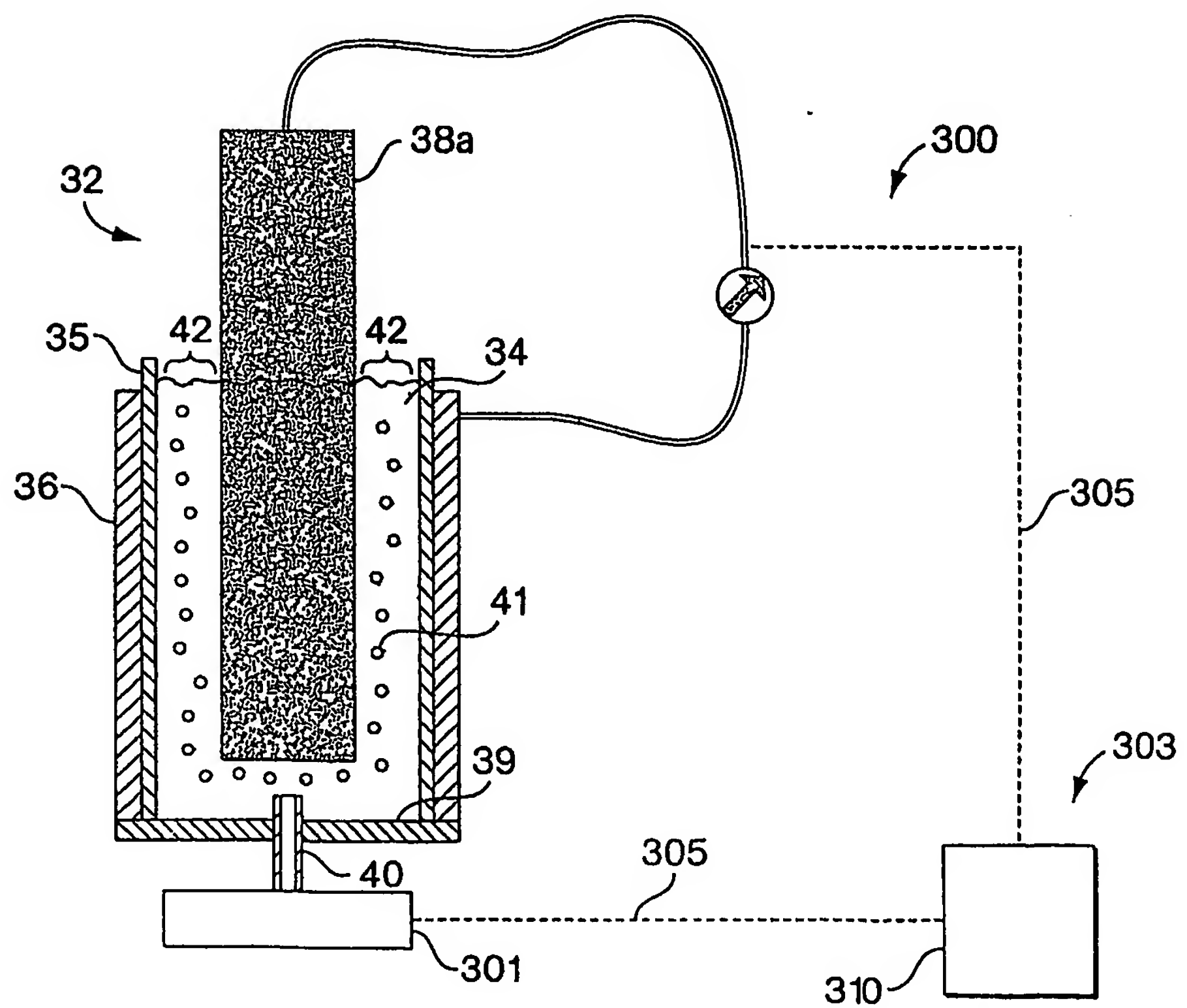


Fig. 10

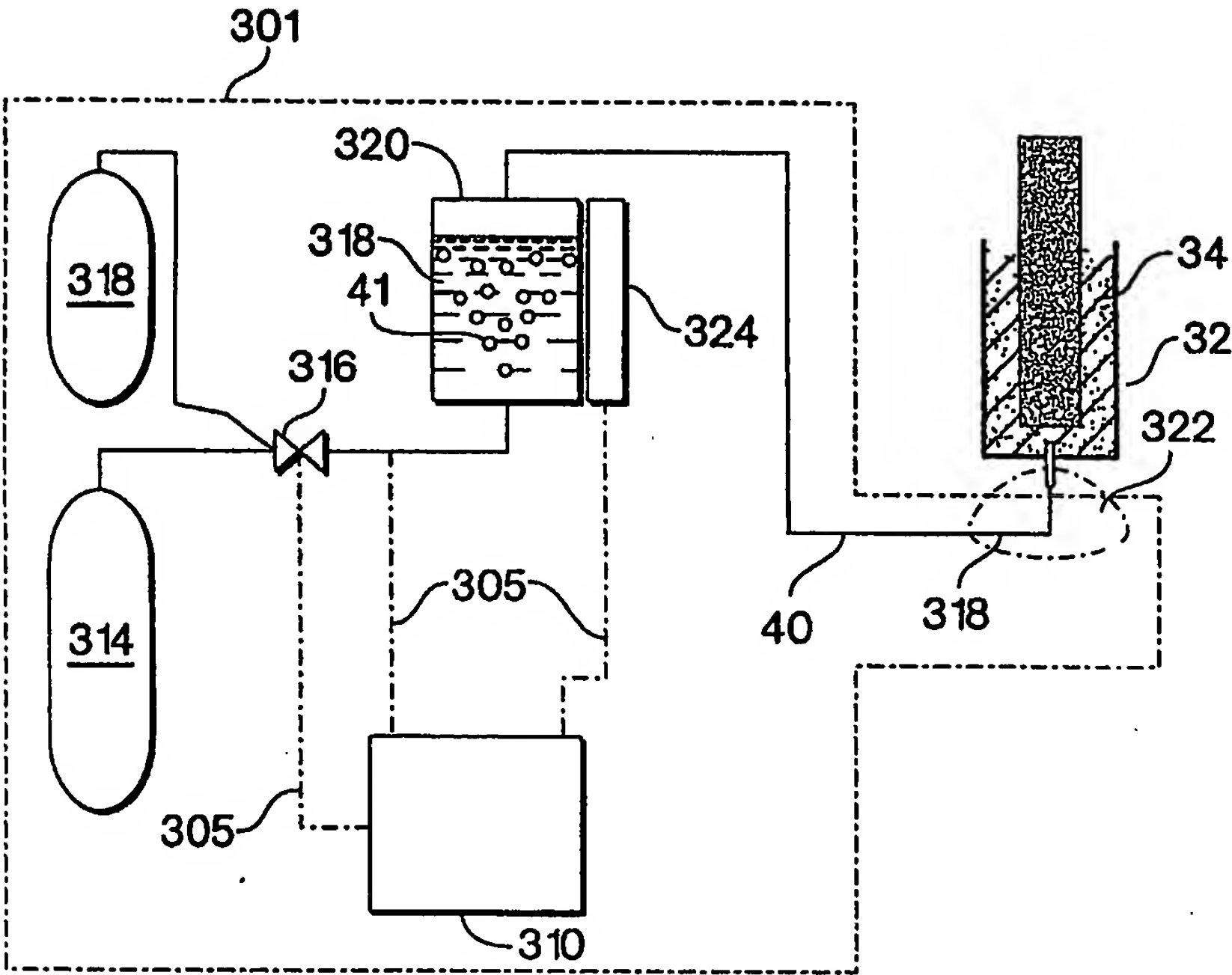


Fig. 11

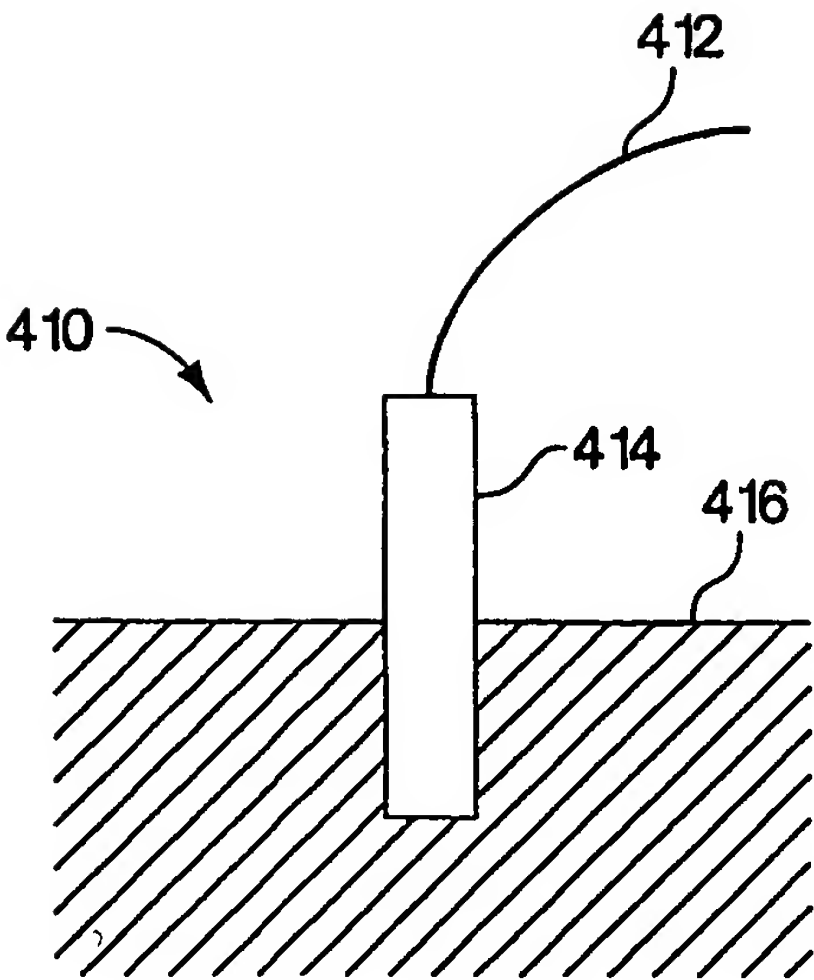


Fig. 12

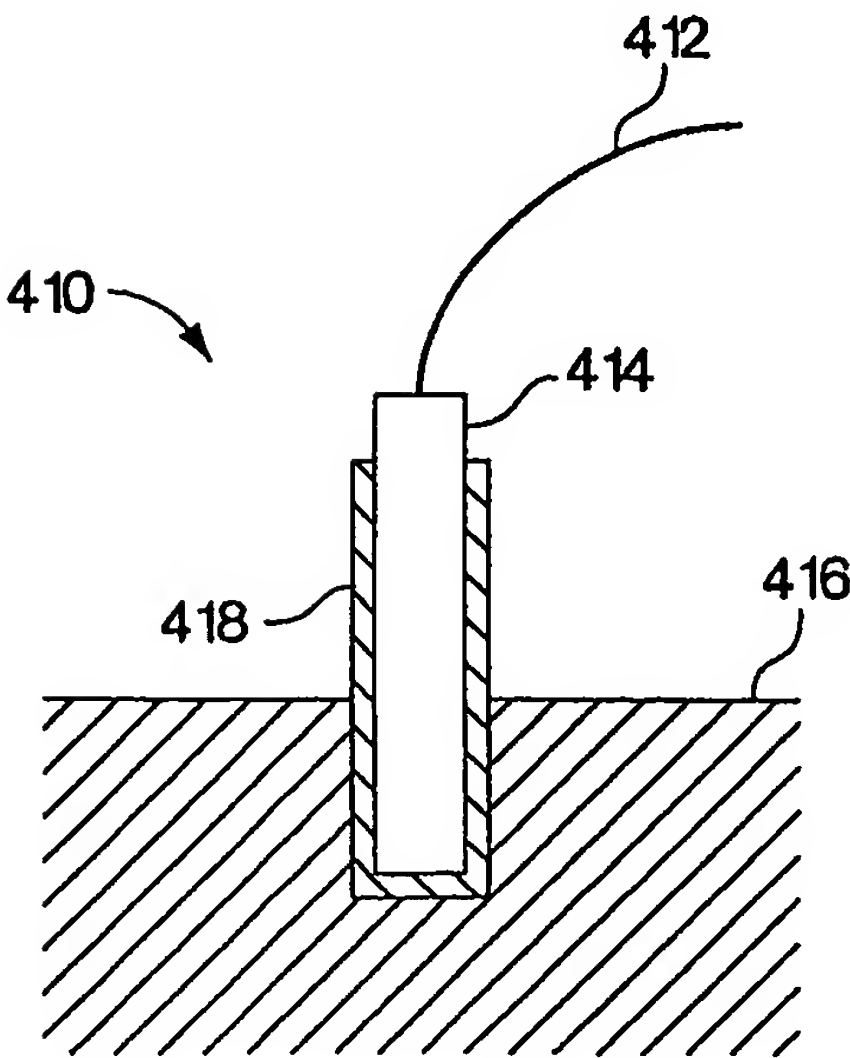


Fig. 13

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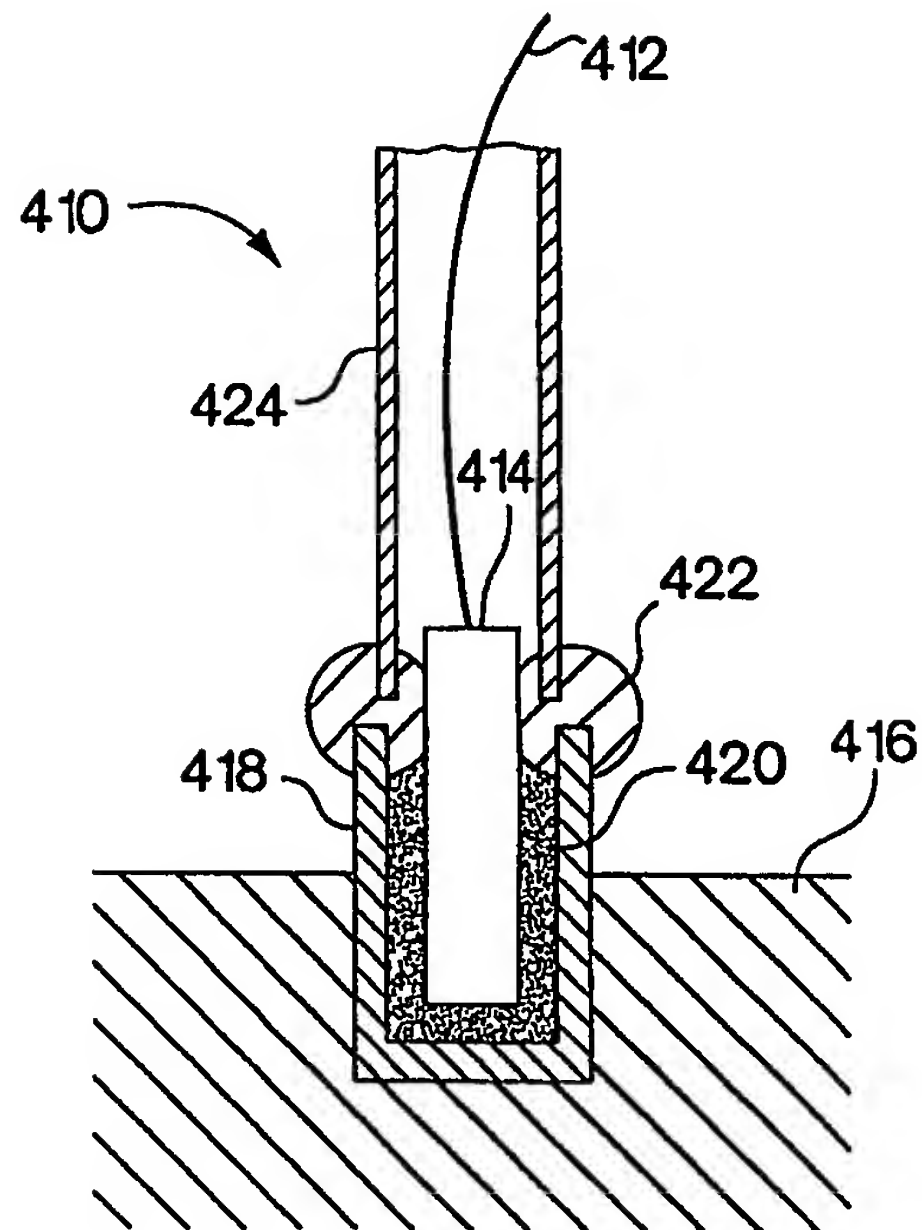


Fig. 14

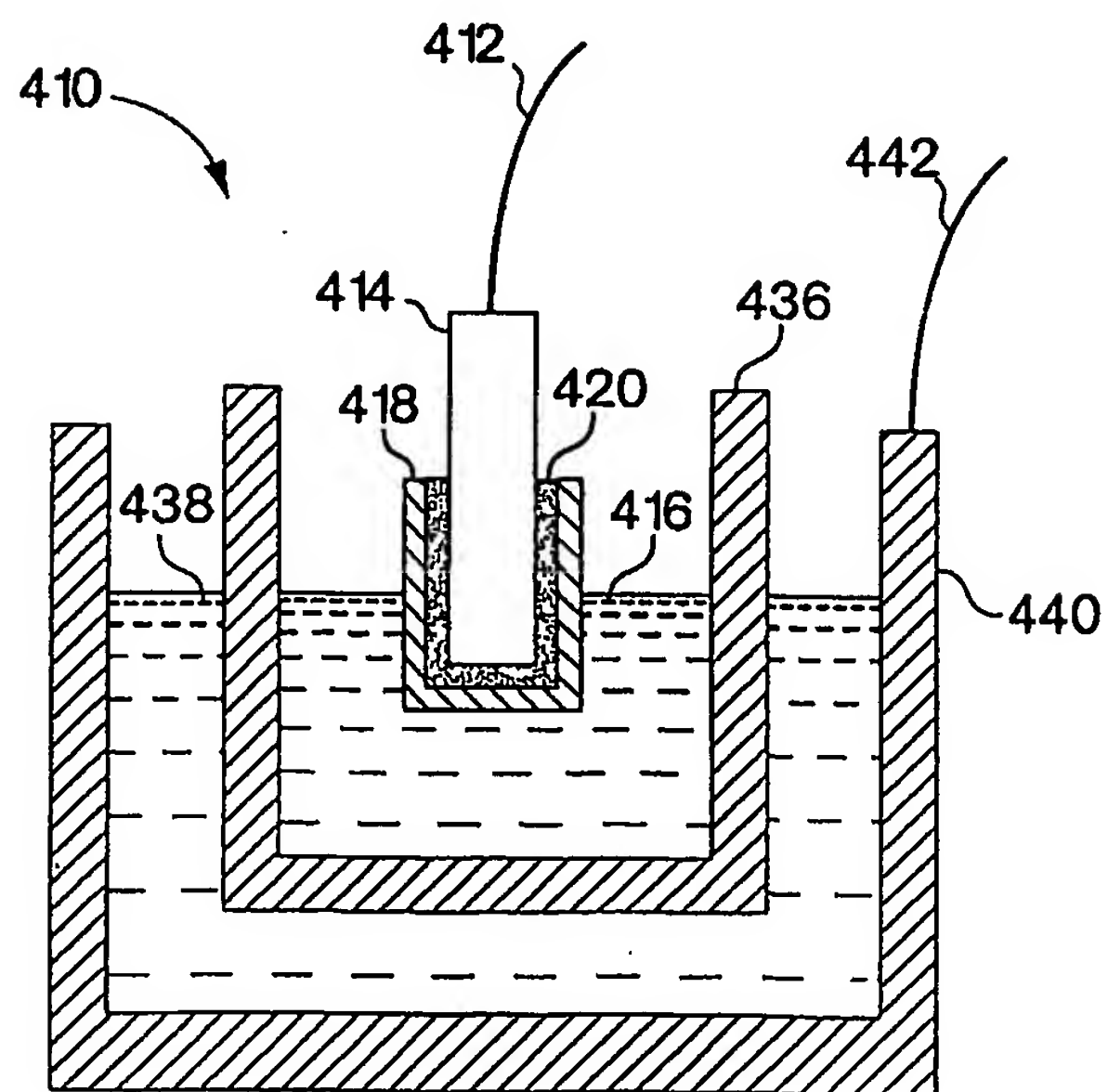


Fig. 15

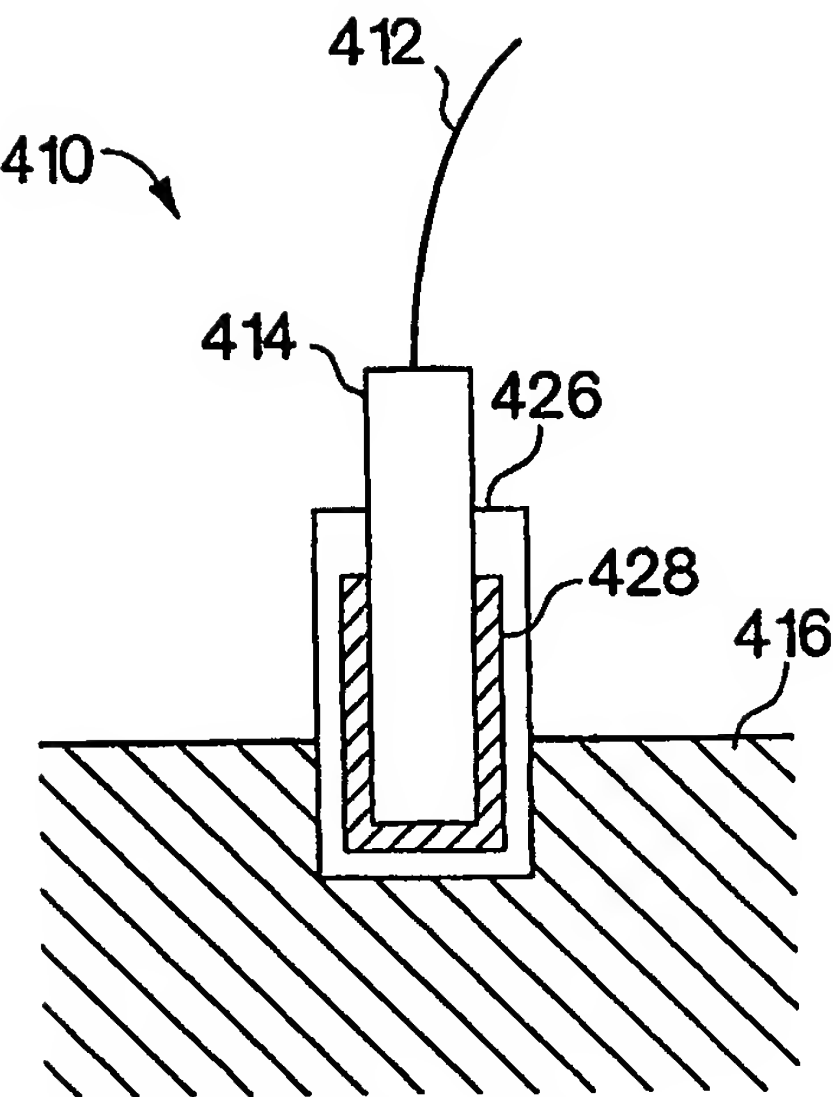


Fig. 16

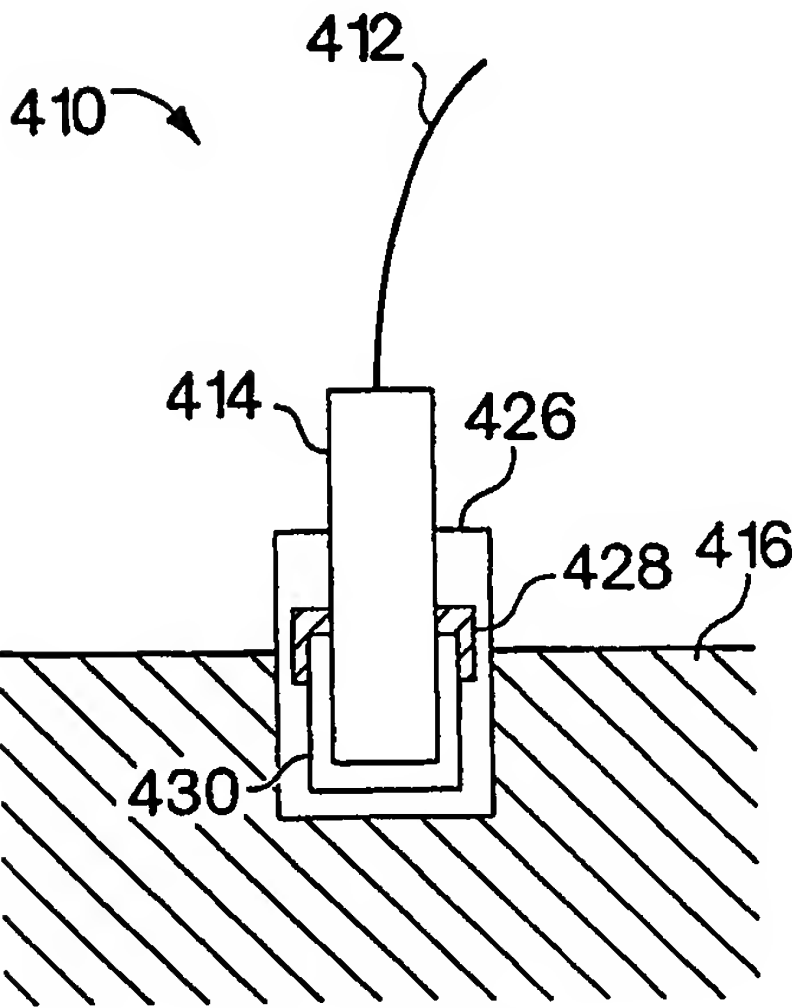


Fig. 17

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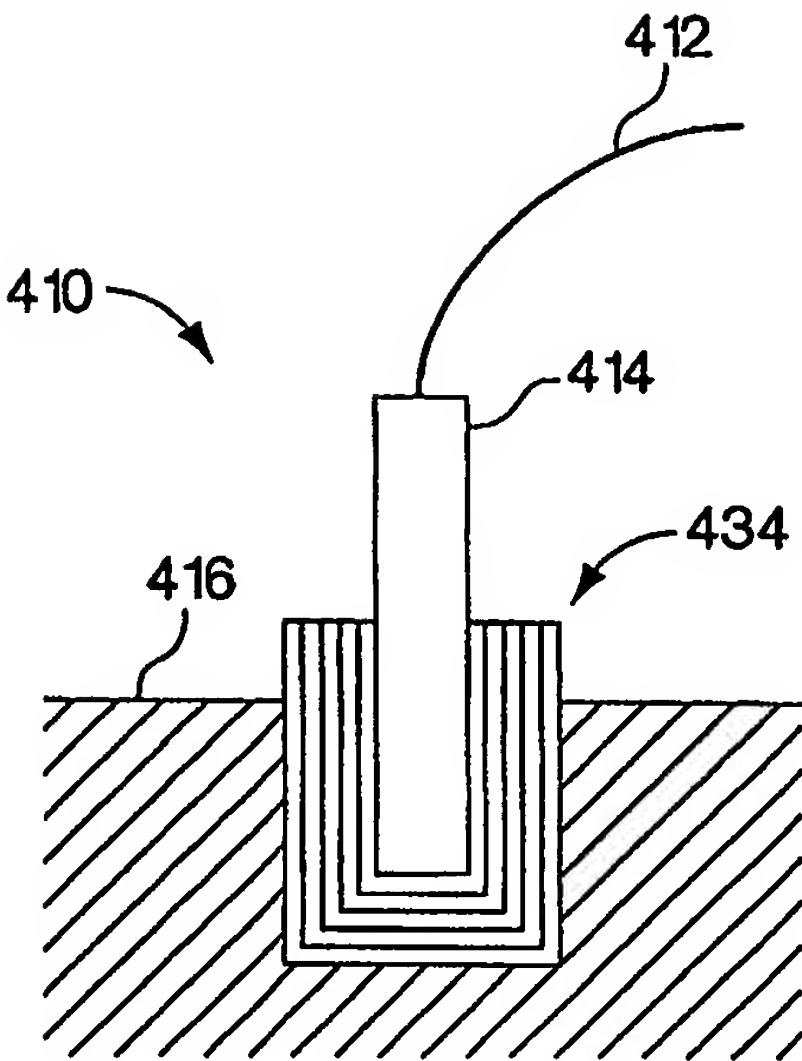


Fig. 18

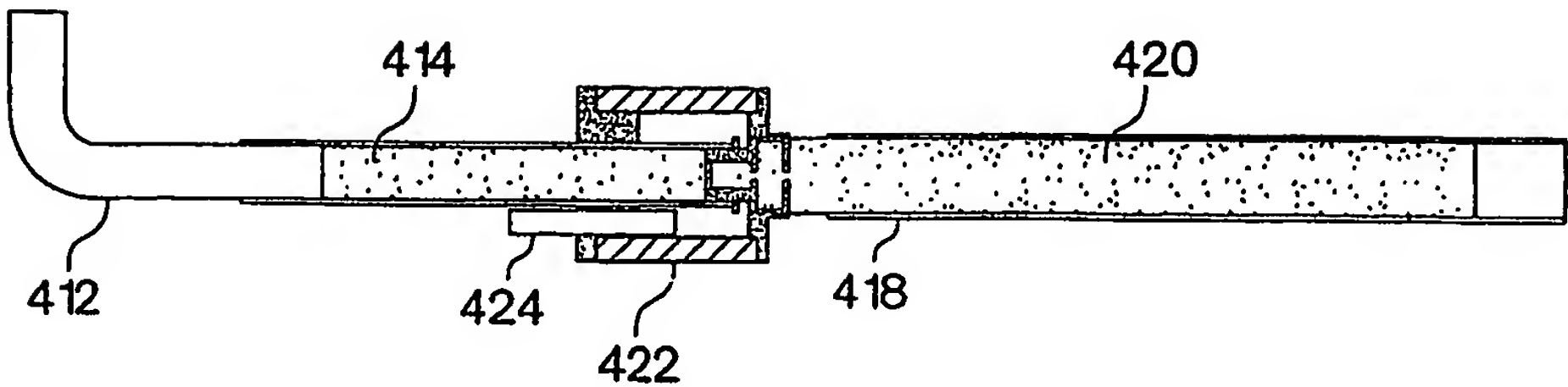


Fig. 19

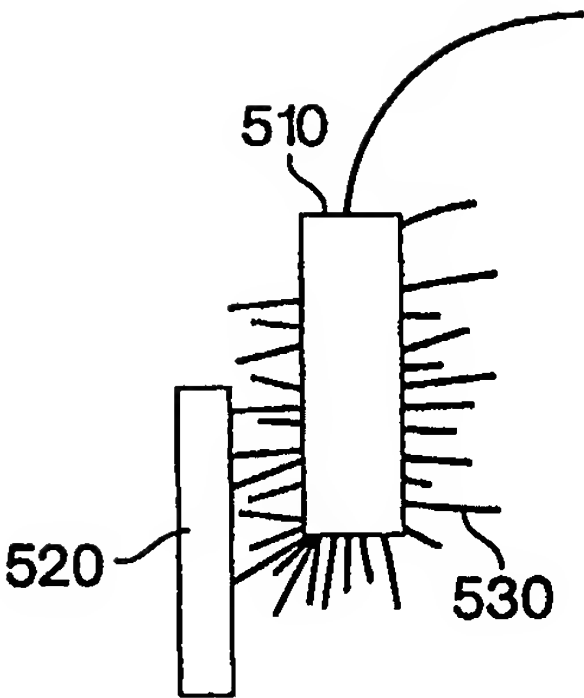


Fig. 20

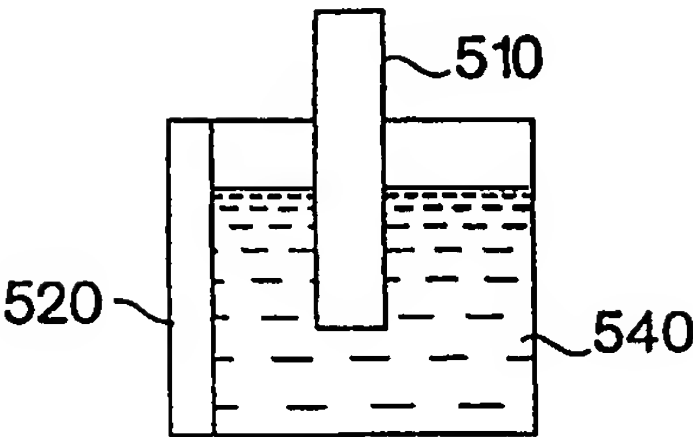


Fig. 21

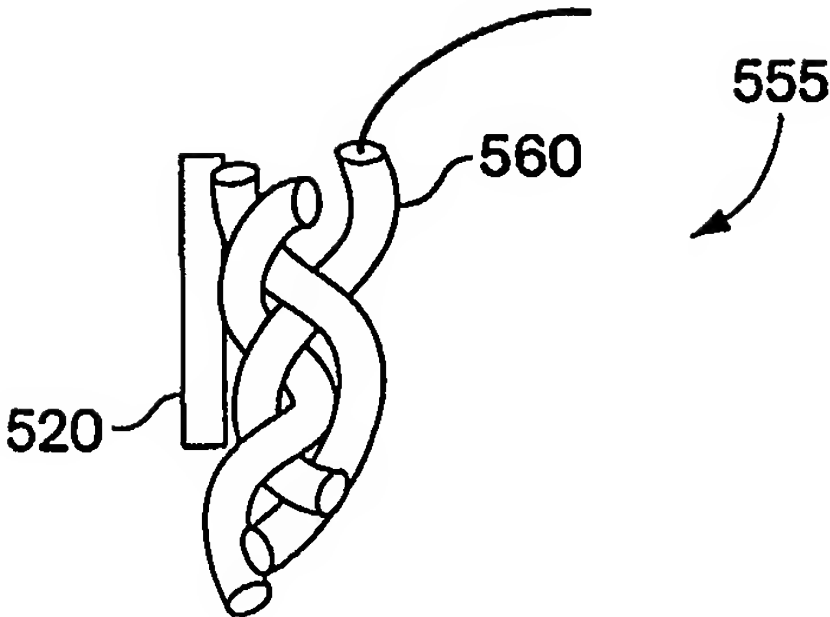


Fig. 22

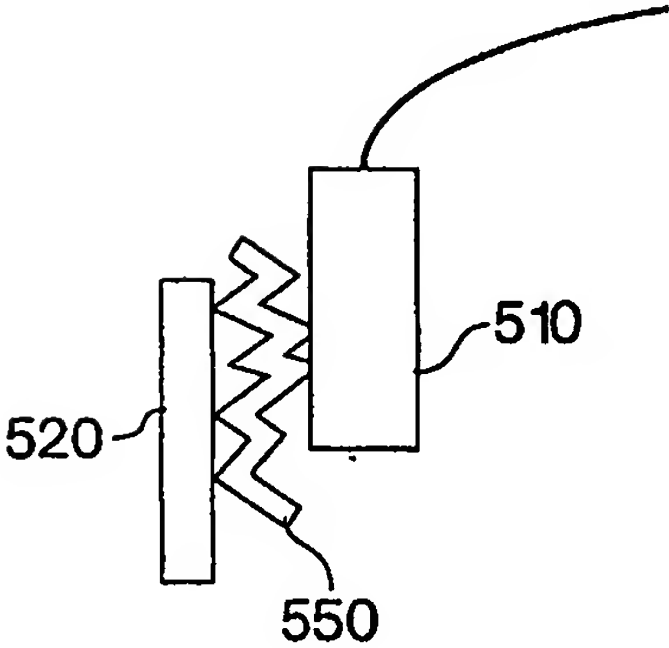


Fig. 23

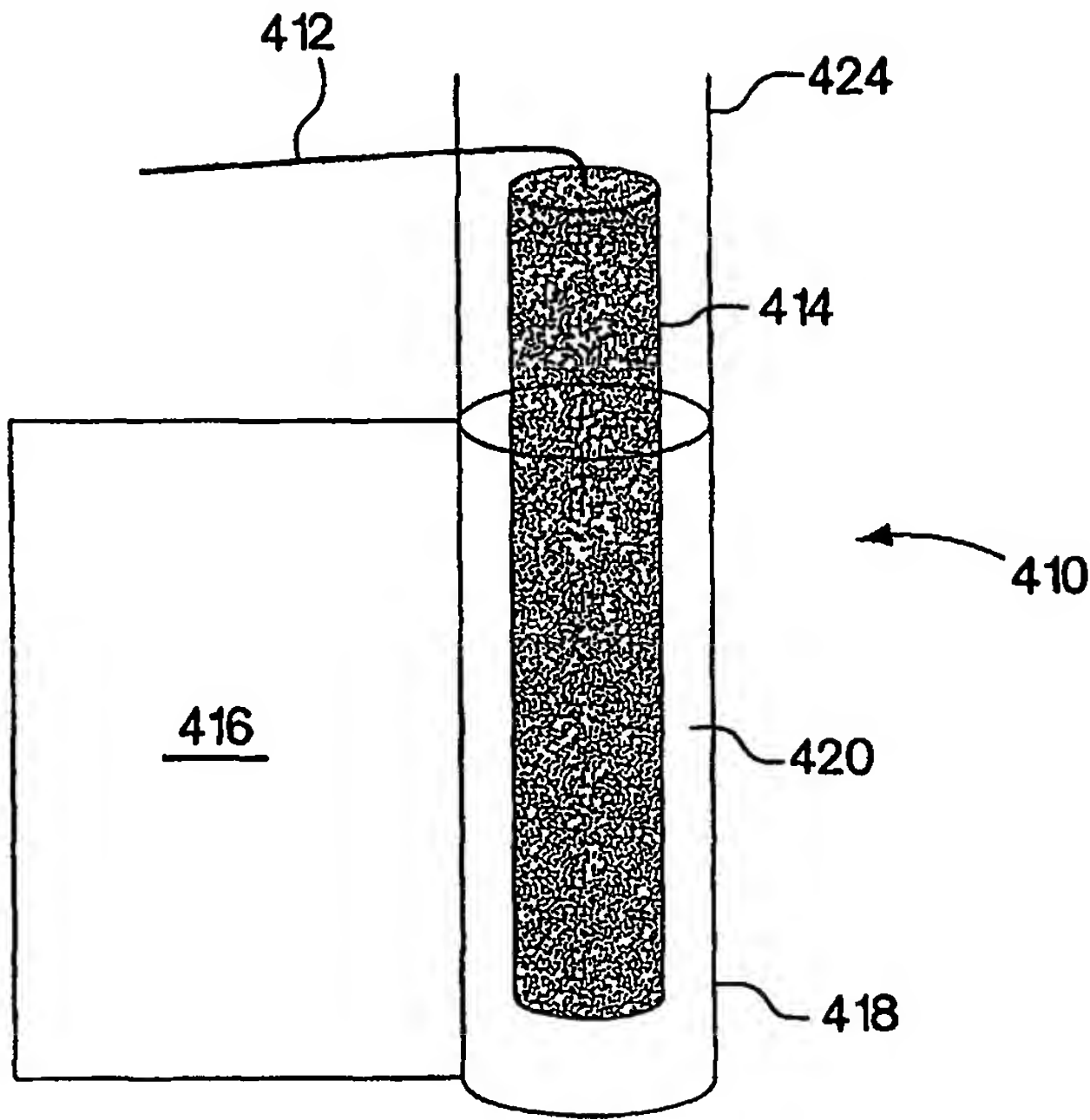


Fig. 24

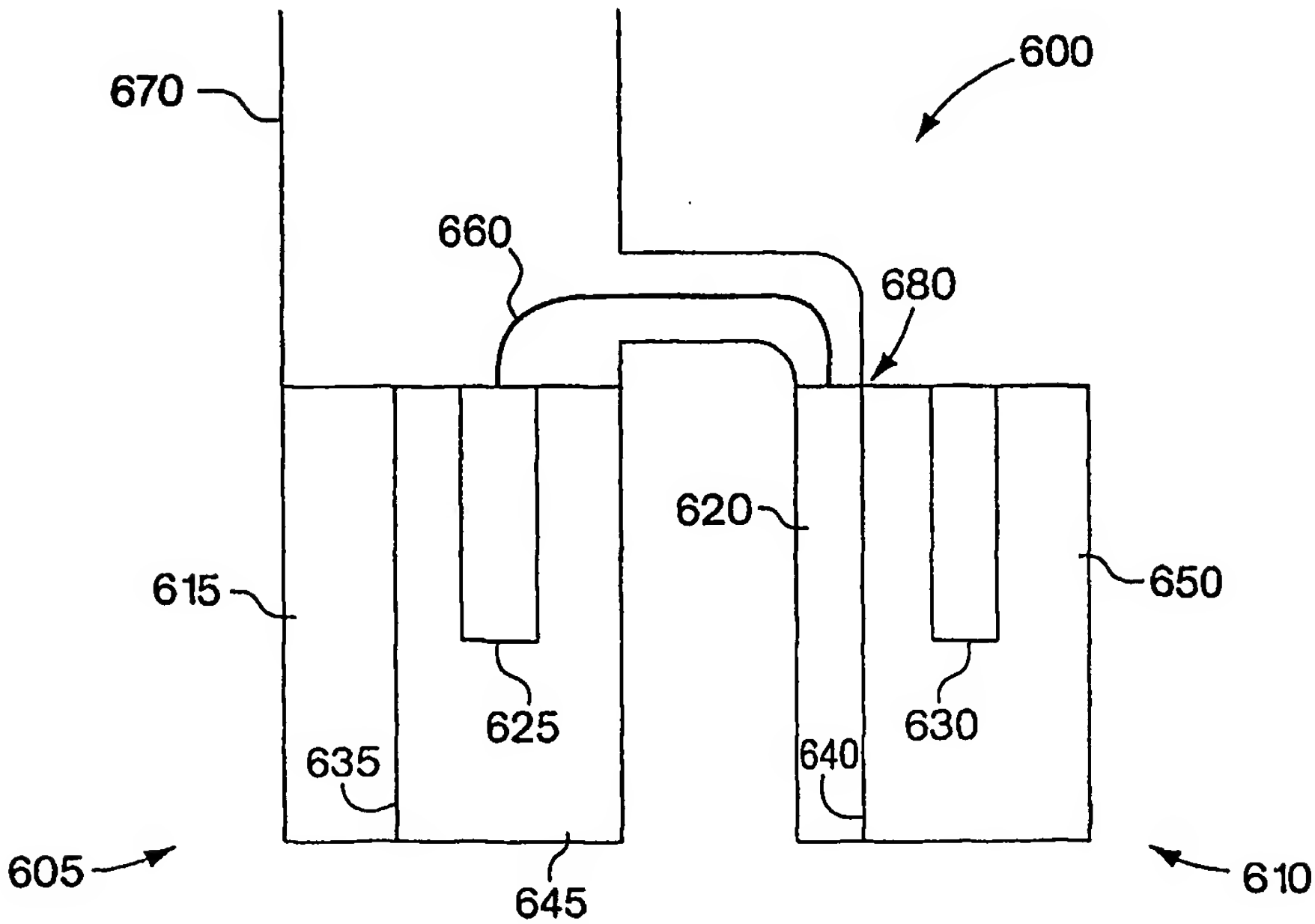


Fig. 25

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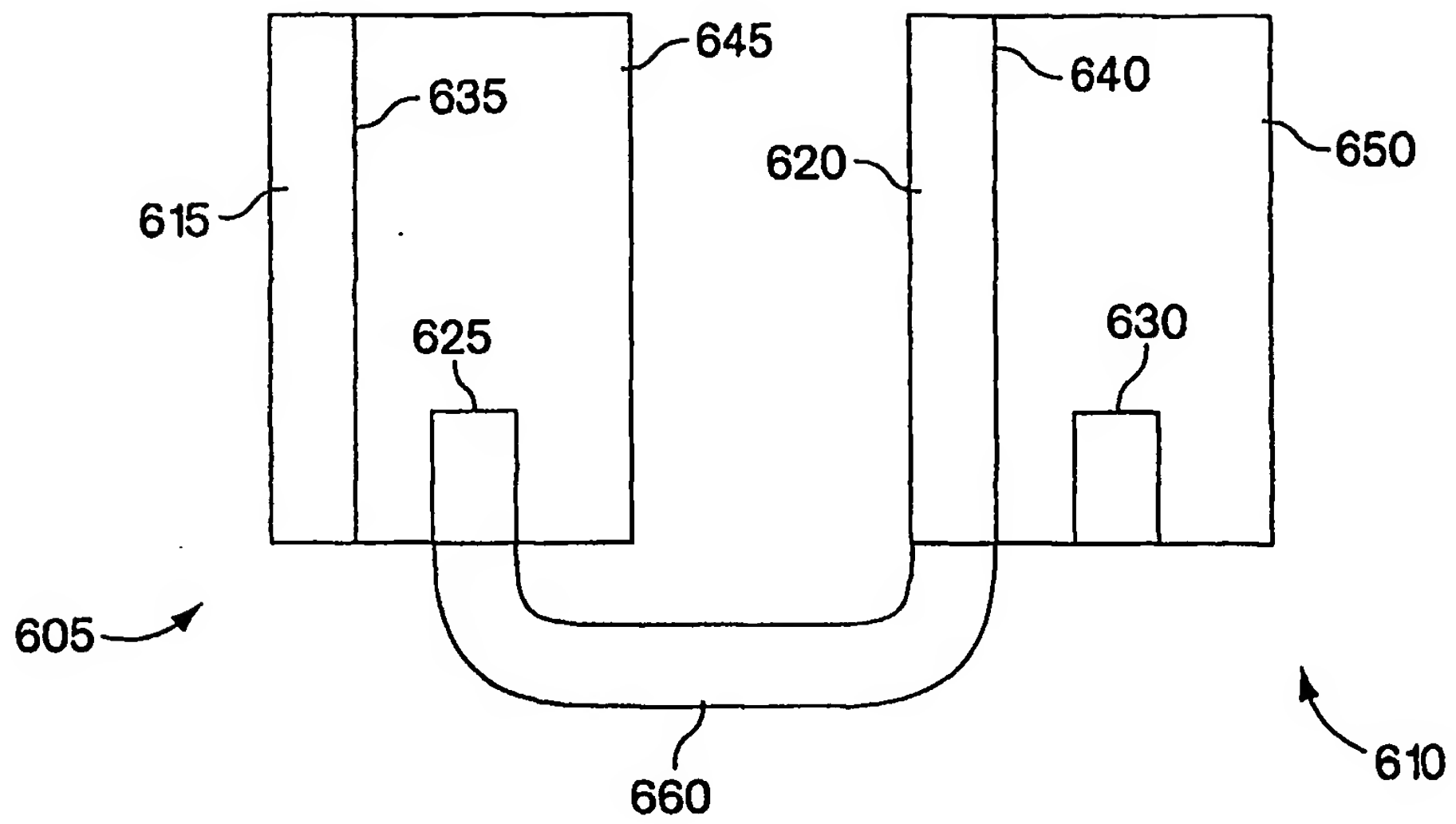


Fig. 26

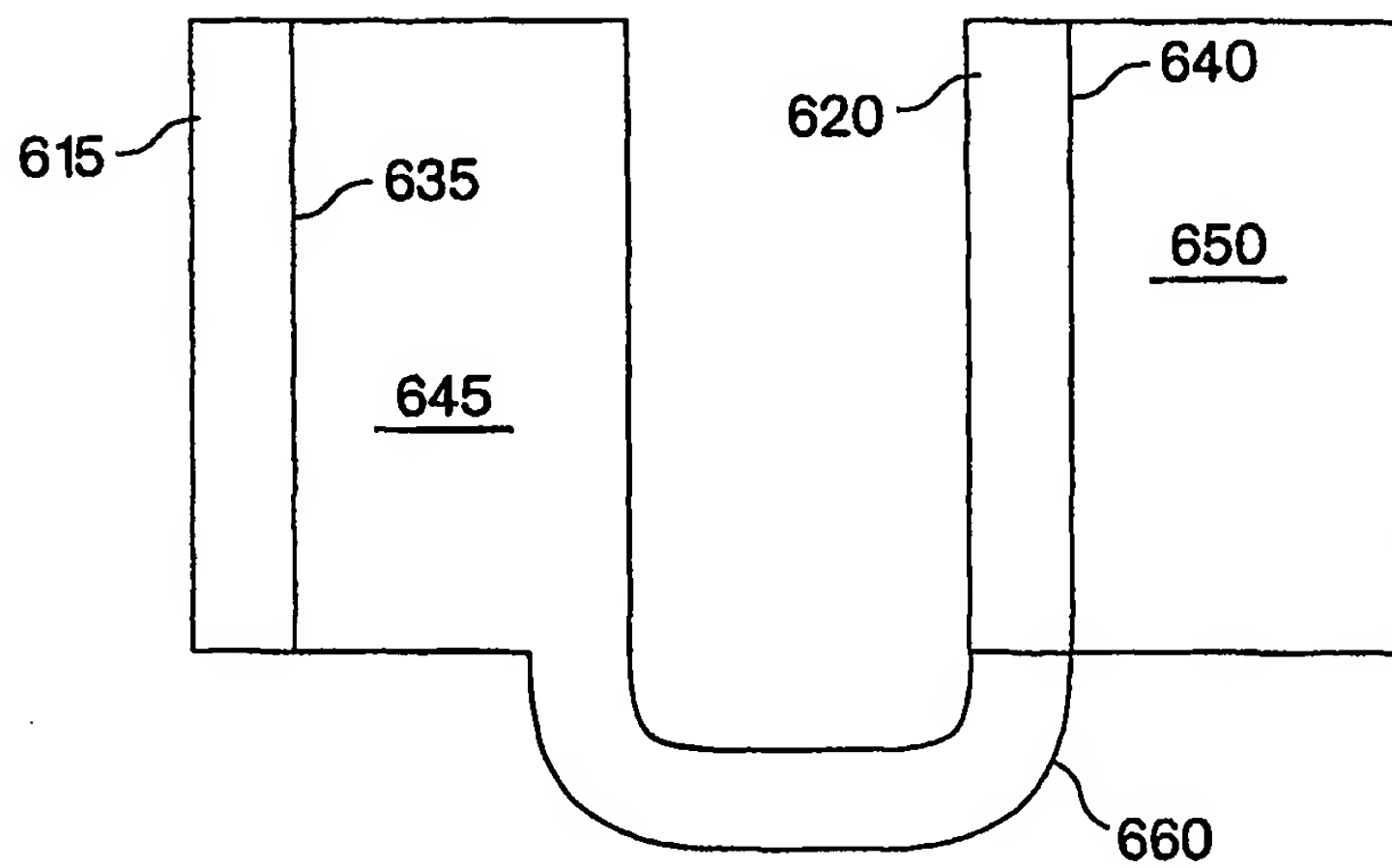


Fig. 27

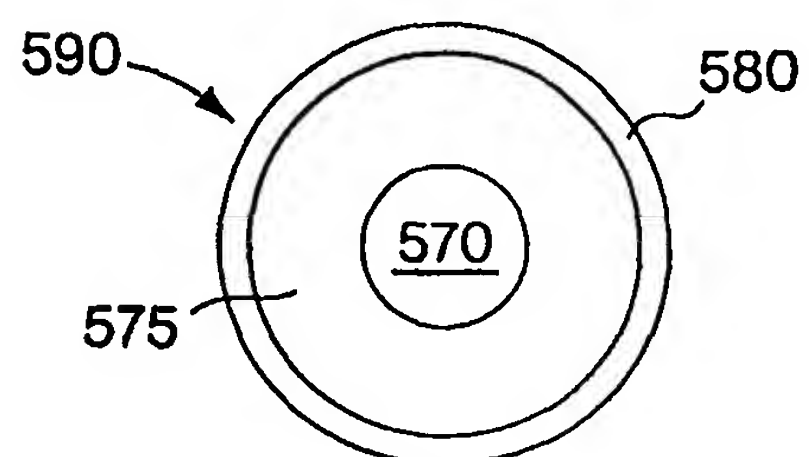


Fig. 28